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Thermal Degradation of Polystyrene. Part II

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PRODUCTION OF MONOMER

It was pointed out in Part I (1) that monomer is produced during degradation in quantities which are 10^3 to 10^4 times larger than the theory of random breaking predicts.

Figure 1 shows the loss in weight, in moles of monomer per base mole, and also the decrease in limiting viscosity with time, of sample G at 288° and 307°C. in vacuo. The experiments on the loss in weight were carried out in a molecular still (see Fig. 2). (An apparatus which allows one to follow the loss of weight continuously will be described in a subsequent paper.) The still was made of Pyrex glass. It consists of a vessel (I) into which the condenser (II) can be inserted, the apparatus being made vacuum-tight by means of a ground-glass joint (III). The condenser was silvered to reduce the effect of heat radiation to a minimum, and cooling was achieved by an acetone-solid carbon dioxide mixture. A small Pyrex vessel containing the substance was placed at the bottom of (I) and the still heated by means of a vapor bath.

It is seen that the curves for the decrease in weight and viscosity (Fig. 1) show a similar behavior. When the rate of decrease of the limiting viscosity slows down, the rate of production of monomer is slowing down as well, and both come eventually to a standstill. This behavior can be explained if one assumes that the formation of monomer is dependent on the rupture of the chain at a weak point. As soon as a link is ruptured, a number of monomer units are broken off the newly formed chain ends until these active chain ends are deactivated.

This reaction may then be considered analogous to the polymerization process in so far as each consists of three steps: (1) The initial break at a weak point whereby two active chain ends are formed (initiation reaction); (2) The splitting off of monomer units from these active chain ends (propagation reaction); and (3) The deactivation of the chain ends, thus terminating the splitting off of monomer units (termination reaction):

$$(1) \qquad +\frac{dc^x}{dt} = -2\,k_R w \qquad \text{Initiation}$$

$$(2) \qquad +\frac{d\,(\text{monomer})}{dt} = -k_2 c^x \qquad \text{Propagation}$$

$$(3) \quad -\frac{d\,c^x}{dt} = k_s c^x \qquad \text{Termination}$$

where w is the number of weak points in the system, and c^x the concentration of active chain ends.

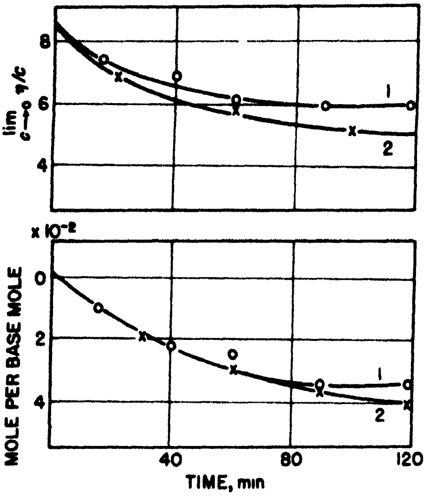


Fig. 1. Decrease of limiting viscosity with time and simultaneous formation of monomers in vacuo - G. (1) 280°C. (2) 307°C.

The order of the termination reaction cannot be decided at this juncture, but, for the sake of simplicity, a first-order termination was chosen.

When the stationary state is reached, one has:

$$2k_R w = k_s c^x$$

Hence:

$$c^x = \frac{2\,k_R w}{k_s}$$

And:

$$\frac{d\,(\text{monomer})}{dt} = -\frac{2\,k_2}{k_s} w$$

The rate of monomer units produced per chain is then:

$$\frac{d\,(\text{monomer})}{dt} = -\frac{2\,k_2}{k_s} k_R S \qquad (\text{cf. Part I})$$

$$= -\frac{2\,k_2 ds_1}{k_s dt}$$

or, for one base mole of polymer:

$$\frac{d\,(\text{monomer})_{\text{moles}}}{dt} = -\frac{2\,k_2}{k_s}\frac{1}{P_0}\frac{ds_1}{dt}$$

or:
$$(\text{monomer})_{\text{moles}} = \frac{2\,k_2}{k_3}\,\frac{1}{P_0}\,s_1 \tag{a}$$

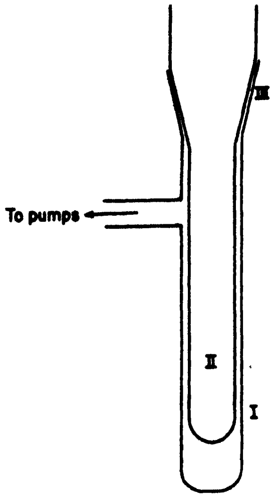


Fig. 2. Molecular still used for experiments on loss of weight.

The amount of monomer in moles, obtained from one base mole of polymer plotted against s_1 should, therefore, give a straight line, the slope of which should then give the amount of monomer in moles obtained from one base mole of polymer per weak link ruptured per original chain.

As Figure 3 shows, straight lines are obtained for an appreciable part of the reaction. The number of monomer units produced per active chain end can be obtained as follows: The amount of monomer obtained per weak link ruptured is 2.4×10^{-2} mole/base mole at 280°C., and 1.88×10^{-2} mole/base mole at 307°C. The original chain length of the material is 1050 (G), hence, 1/1050 mole of polymer produces 2.4×10^{-2} mole of monomer at 280°C., and 1.88×10^{-2} mole of monomer at 307°C., per weak link ruptured. One can also express these quantities in monomer units obtained per weak link ruptured, or per active chain end. At 280°C., 19.7 monomer units and, at 307°C., 12.6 monomer units are obtained per weak link ruptured; half of these quantities are therefore produced per active chain end.

Table I shows the moles of monomer produced from 1 base mole of material and the number of moles one would expect according to the theory of random breaking of bonds. It is seen that the amount of monomer produced is about 10^3 to 10^4 times larger than that required by theory.

DEGRADATION OF POLYSTYRENE IN PRESENCE OF AIR

Several experiments were carried out to show the influence of oxygen on the thermal degradation of polystyrene. As mentioned pre-

viously, oxygen has a profound influence on the degradation, the reaction taking place at about the same rate as the one in vacuo at a temperature about one hundred degrees lower. The experiments were carried out in long open tubes containing 0.1 to 0.5 g. of substance. Fraction F_{III}, having a $\lim_{c \to 0} \eta_{sp}/c = 9.1$, was employed, the tubes were kept in vapor baths; they were withdrawn at definite time intervals, and the limiting viscosities were ascertained. The experimental results are represented in Figure 4, in which the limiting viscosities are plotted against the time in minutes. Curves suitable for a kinetic analysis could not be obtained at temperatures above 220°C. since the oxidation is already too violent in this region of temperatures; many side reactions set in and the material quickly becomes yellow and brown.

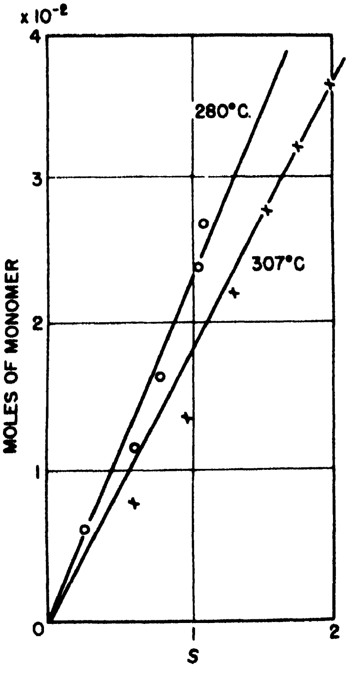


Fig. 3. Moles of monomer formed per base mole of polymer in dependence on number of average breaks per initial chain.

TABLE I. Comparison of Amounts of Monomer Obtained from One Base Mole Polymer According to the Theory of Random Breaking and Experiment ($P_0 = 1000$, G)

Average number breaks per chain	Moles monomer per base mole polymer	
	theor.	Exp.
0.5	1.30×10^{-6}	0.8×10^{-2}
1.0	3	1.5
2.0	8	4.0

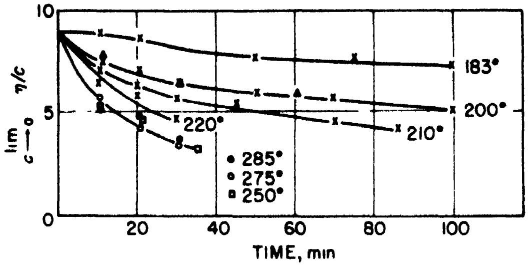


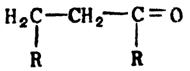
Fig 4. Decrease of limiting viscosity with time during degradation in presence of air (F_{III}). Δ indicates diffusion experiments.

It is reasonable to assume that the first stage of the oxidation consists in the formation of hydroperoxide groups (cf. Farmer (1a)), which leads eventually to chain scission. If one works out a mechanism on these lines and compares it with the experimental results, it is found that degradation in the presence of oxygen is also slowed down in its later stages. It is likely, therefore, that inhibitors in the form of antioxidants may be formed during degradation. Experiments on the inhibition of degradation show that antioxidants are effective; among these is benzaldehyde, which is known to be produced during degradation of polystyrene in air. Table II shows a number of experiments on inhibition; it may be remarked that the same class of substances that inhibits polymerization also inhibits degradation.

We can assume, therefore, that inhibitors, which cause the slowing down of the reaction, are formed during the degradation, and a reaction scheme can be formulated as follows:

Polystyrene + O_2
⇅
Polystyrene hydroperoxide
↓
Chain scission
↓
Inhibitors
↓
Decay of inhibitors

In support of the assumption that inhibitors are formed during degradation, a passage from a paper by Votinov, Kobeko, and Marey (2) on the depolymerization of linear polymers may be quoted. This paper will be discussed in more detail in a subsequent section. "When polystyrene is heated in air, oxidation takes place with formation of ketones of this type:



$$\underset{\textstyle R}{\underset{|}{H_2C}}-CH_2-\underset{\textstyle R}{\underset{|}{C}}=O$$

TABLE II. Action of Antioxidants (0.05 g. of G Heated 60 Min. at 200°C. in Air; $\lim_{c \to 0} \eta/c$ before Heating, 8.3)

No.	Test condition	$\lim_{c \to 0} \eta/c$	Heating, time, min.
1	Small amount of beta-naphthol	6.0	60
2	Without addition	4.5	60
3	Large amount of benzaldehyde	8.1	60
4	Some benzaldehyde	7.6	30
5	Without addition	5.7	30

By means of distillation it was ascertained that it contained about 80% of monomer. The resulting depolymerized styrene monomer is poisoned by some kinds of polymerization inhibitors, from which it can be freed only by very thorough cleansing. The monomer newly obtained by depolymerization practically does not polymerize and thickens a little only in the presence of very active catalysts of the organometallic type."

The whole process can then be written as follows:

(1) $$+\frac{d[\text{per.}]}{dt} = -k_1[O_2][n]$$ Oxidation

(2) (a) $$\frac{-d[\text{per.}]}{dt} = k_2[\text{per.}]$$ Peroxide decomposition

(b) $$-\frac{d[\text{per.}]}{dt} = k_3[\text{per.}]$$ Chain scission

(c) $$-\frac{d[\text{per.}]}{dt} = k_4[\text{per.}][i]$$ Inhibition

(3) (a) $$+\frac{d[i]}{dt} = k_5[\text{per.}]$$ Formation of inhibitor

(b) $$-\frac{d[i]}{dt} = k_6[X][i]$$ Decay of inhibitor

For the initial stages of the reaction, when [i] is negligible, one obtains:

$$k_1[O_2][n] = k_2[\text{per.}] + K_3[\text{per.}]$$

$$[\text{per.}] = \frac{k_1[O_2][n]}{k_2 + k_3} \simeq \frac{k_1}{k_2}[O_2][n]$$

Hence (2b):
$$-\frac{d[\text{per.}]}{dt} = +\frac{dw_R}{dt} = \frac{k_3k_1}{k_2+k_3}[O_2]\,[n]$$

Or:
$$w_R = \frac{k_3k_1}{k_2 + k_3}[O_2]\,[n]\,t$$

We have, then, for a single chain:

$$\frac{s_1}{P_0} = \alpha' = k_I t$$

where:
$$k_I = \frac{k_3k_1}{k_2 + k_3}[O_2] \qquad \text{(b)}$$

One obtains, therefore, a straight line for the initial stages of the reaction - which is approximately the case, as Figure 5 shows.

As the concentration of the inhibitor increases during the course of the reaction, the degradation slows down until the concentration of the inhibitor becomes constant. When this stage is reached, one obtains a relationship:

$$k_1[O_2]\,[n] = k_2[\text{per.}] + k_3[\text{per.}] + k_4[\text{per.}]\,[i]_{\text{final}}$$

From this, finally:

$$[\text{per.}] = \frac{k_1}{k_3 + k_2 + k_4[i]_{\text{final}}}[O_2]\,[n]$$

Hence (2b):
$$-\frac{d[\text{per.}]}{dt} = \frac{dw_R}{dt} = \frac{k_3k_1}{k_2 + k_3 + k_4[i]_{\text{final}}}[O_2]\,[n]$$

or:
$$w_R = k_{II}t = k_I\frac{1}{1 + b}[n]\,t$$

where:
$$b = \frac{k_4[i]_{\text{final}}}{(k_2 + k_3)}$$

or, for a single chain:

$$\frac{s_1}{P_0} = \alpha' = K_{II}t = K_I\frac{1}{1 + b}t \qquad \text{(c)}$$

Figure 5 shows that the reaction eventually slows down and gives the straight-line relationship required by equation c.

The intermediate region is given by:

$$\frac{ds_1}{dt} = -K_I \frac{P_0}{1 + f(i)}$$

where f(i) is a function of the inhibitor concentration. For f(i) = 0, this equation becomes identical with equation b, and for the later stages when f(i) becomes constant, with equation c.

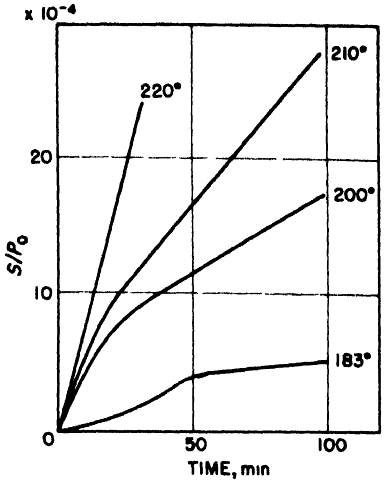


Fig. 5. Degree of degradation against time in the presence of air.

Log K_I is plotted against 1/T in Figure 6, the slope giving 26.2 kcal. K_I and K_{II} are also tabulated in Table III, and K_{II} is plotted against 1/T in Figure 6, giving 29.9 kcal.

A question arises in this connection. It may be argued that the slowing down of the reaction may be due to a diffusion process. It may be imagined that oxygen dissolved in the polymer is used up during the

TABLE III. Degradation in the Presence of Air for Fraction F_{III}

Temperature, °C.	k_I, min^{-1}	k_{II}, min^{-1}
220	7.6×10^{-5}	-
210	5.6	2.3×10^{-5}
200	4.0	1.2×10^{-5}
183	1.2	3.7×10^{-6}

initial stages, and that the diffusion of oxygen then becomes the rate-determining step. That this is not the case was shown as follows. First, a certain amount of polymer was degraded, exposing only a small area to the air, and, second, another sample of the same polymer and of equal weight was degraded in the form of a film, exposing to the air an area about ten times larger than in the first case. The polymer film was obtained by evaporating a polystyrene solution in benzene. As Table IV and Figure 4 show, the rate of degradation is the same in both cases, indicating that diffusion has no influence under these experimental conditions. It also shows that the Pyrex glass surface does not act catalytically upon the reaction. Diffusion will, of course, become of importance in cases involving larger amounts of polymer.

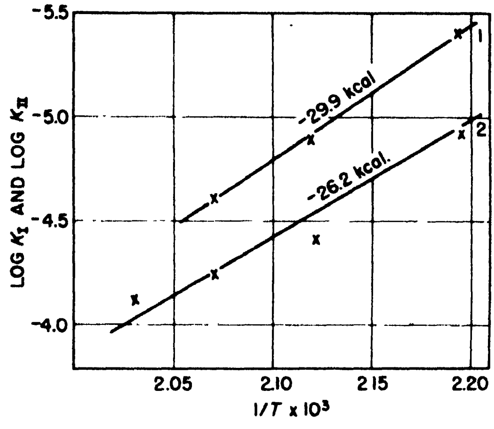


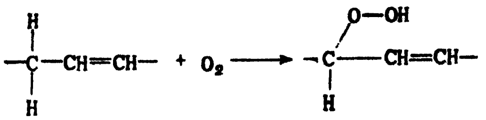
Fig. 6. Energies of activation for degradation in the presence of air (1) log K_{II} against 1/T; (2) log K_I against 1/T.

TABLE IV. Diffusion Experiment for Fraction F_{III} in air at 200°C.

t, min.	$\lim_{c \to 0} \eta/c$ film	$\lim_{c \to 0} \eta/c$ bulk
0	9.1	9.1
10	7.9	7.7
30	6.6	6.6
60	6.0	-
70	-	5.8

ELEMENTARY STEPS

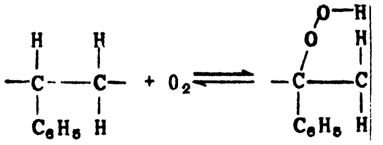
Farmer and co-workers (1a) have recently demonstrated, in various investigations, that the first step in the oxidation of olefinic hydrocarbons consists in the formation of hydroperoxide groups at the alpha-methylenic bond, thus:



(d)

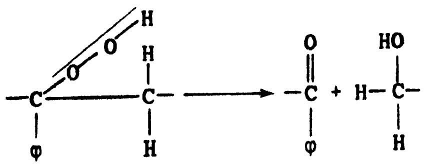
Subsequent reactions lead either to chain scission or to destruction of the hydroperoxide groups without rupturing the main chain (e.g., formation of hydroxyl groups).

The corresponding reactive points in polystyrene are the alpha-carbon atoms, the first step in the oxidation of polystyrene being depicted as follows:



(e)

Some of these hydroperoxide groups will then bring about chain scission, with the formation of keto and hydroxyl groups:

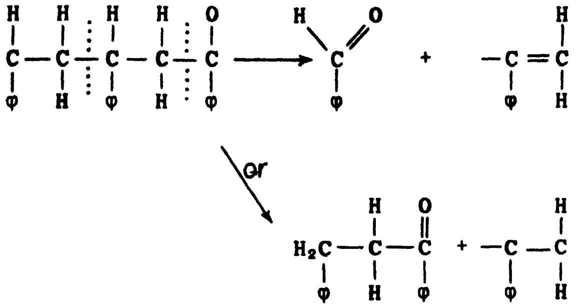


(f)

Other hydroperoxide groups will undergo secondary changes which will not lead to chain scission.

It is interesting to compare in this connection the conclusions reached by Jackson and Forsyth (3) in their investigation of the power factor of polythene heated in the presence of oxygen. They conclude that the initial attachment of oxygen to polythene consists in hydroxyl or hydroperoxide groups. The presence of such groups has been established in the case of oxidized polythene. These groups give rise to chain scission and also to cross linking depending upon the amounts of oxygen present.

Inhibitors may be formed by breaking off these oxidized chain ends and forming, for example, benzaldehyde, - which was actually found by Staudinger (compare also Votinov, Kobeko, and Marey mentioned above) in degraded products, and which was shown in a previous section to have a retarding influence on the degradation:



(g)

(h)

The inhibitors formed during degradation in the presence of oxygen will retard the reaction by destroying the peroxides, which must have a life time long enough to permit the inhibiting molecule to come into contact with them. The inhibitor itself may be oxidized to a peroxide which can then react with the peroxide at the polystyrene chain, leading to destruction of both these peroxide groups. Alternatively, the inhibitor may become a peroxide by reacting with the polystyrene peroxide, and then these groups may destroy each other. Compare, in this connection, Dufraisse and co-workers (4).

Acknowledgment

The author wishes to thank Professor E. K. Rideal, F.R.S., for stimulating discussions and advice given throughout this work. Thanks are also due to B. X. Plastics Ltd., for financial assistance.

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Synopsis

The production of monomer during degradation of polystyrene in vacuo below 310°C. has been investigated. A mechanism has been proposed which explains the dependence of monomer formation on the initial breaks in the chain. The degradation in presence of oxygen has been studied. A mechanism for this reaction has been proposed which accounts for the type of curves obtained experimentally. The role of antioxidants has been briefly indicated. The elementary steps for the degradation in vacuo and in the presence of oxygen have been discussed.

Résumé

La production de monomère au cours de la dégradation du polystyrol sous vide à une température inférieure à 310° a été etudiée. Un mécanisme est presente pour expliquer la dependance de la formation de monomère aux dépens des ruptures préliminaires dans la chaîne. La degradation en présence d'oxygène a été étudiée. Pour cette reaction également, un mécanisme est proposé pour rendre compte des courbes obtenues expérimentalement. Le rôle des antioxydants est brièvement décrit. Les étapes élémentaires de dégradation sous vide et en présence d'oxygène sont discutées.

Zusammenfassung

Es wird die Bildung des Monomers von Polystyrol im Vakuum unterhalb 310°C. untersucht. Es wird ein Mechanismus vorgeschlagen, der die Monomerbildung mit primärem Kettenabbruch verbindet. Abbau in Gegenwart von Sauerstoff wird studiert und ein Reaktionsmechanismus vorgeschlagen, der die experimentellen Kurven deutet. Die Rolle von Antioxydationsmitteln wird kurz erwähnt. Die Elementarreaktionen fur Vakuum – und Sauerstoffabbau werden diskutiert.

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Thermal Degradation of Polystyrene and Polyethylene. Part III.

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Part I dealt with the degradation of polystyrene in vacuo at temperatures below 340°C. (1). It was pointed out that amounts of monomer 10^3 to 10^4 times larger than those expected from the theory of random breaking of links were produced.

It was thought desirable to present a more detailed elucidation of the formation of monomer and to extend the investigations to higher temperatures, at which this reaction is predominant. An apparatus which allows the production of monomer to be followed continuously has been constructed for this purpose. A discussion of the experimental results, and an attempt to outline the mechanism of degradation for this range of temperatures, will be given below.

Apparatus

The apparatus used is shown in Figure 1. A quartz spring (1) consisting of 5 coils, each of 2-cm. diameter, is connected to a Pyrex ground-glass stopper by means of a quartz Pyrex seal (2). The diameter of the quartz is about 1 mm. A straight quartz beam 1 mm. thick and 54 cm. long is sealed to the spring. This arrangement fits into the Pyrex apparatus shown in Figure 1. It consists of a bulb of 14-cm. diameter to which 4 side tubes are sealed. An electric furnace of 1.8-cm. inner diameter, 3-cm. outer diameter, and 3-cm. height (Duralumin), is fixed to the iron rod (4), separated by a piece of asbestos stone (5) for heat insulation from the iron rod (6). This rod fits into the glass tube (7), which is sealed to the male ground-glass joint (3). The furnace leads are soldered to tungsten wires (8), which are sealed through the glass. The temperature of the furnace can be regulated by the rheostat (9). An ammeter is included in the circuit. The temperature in the furnace is measured by a Chromel-Alumel thermocouple placed inside the furnace as indicated in the diagram. The thermocouple leads (10) are soldered to tungsten wires sealed through the glass. The junctions between the tungsten wires and the potentiometer leads are kept in ice. The platinum or glass reaction vessel (11) (diameter 1 cm., height 1 cm., weight about 0.25 g.) is introduced through the side tube (12) and fixed by means of a platinum wire hook into a notch in the quartz beam. The side tube is then closed by a condenser (13). The bottom of the condenser is 5 cm. from the top of the furnace—a distance that is small compared with the mean free path of molecules the size of monostyrene in a vacuum of 10^{-5} to 10^{-6} mm. Hg. A cooling mixture of solid carbon dioxide and acetone is employed in the condenser. The tube (14) leads to a three-stage mercury diffusion pump backed by a Hyvac rotary oil pump. A spring of glass tubing consisting of two coils of 24-cm. diameter is interposed between the apparatus and the pumps to damp oscillations set up by the latter. The apparatus is insulated from vibrations in the building by rubber disks. The side tube (15) is closed by a plane glass plate of about 4-mm. thickness fixed by picein. A small horizontal pointer is attached to the end of the quartz beam at right angles to it. This pointer is illuminated and can be observed in a telescope fitted with a scale in the eyepiece. Before starting an experiment the quartz beam is held in position by a support (16) indicated in the diagram. This support consists of nickel wire soldered to a piece of tungsten wire sealed into a male ground-glass joint (17).

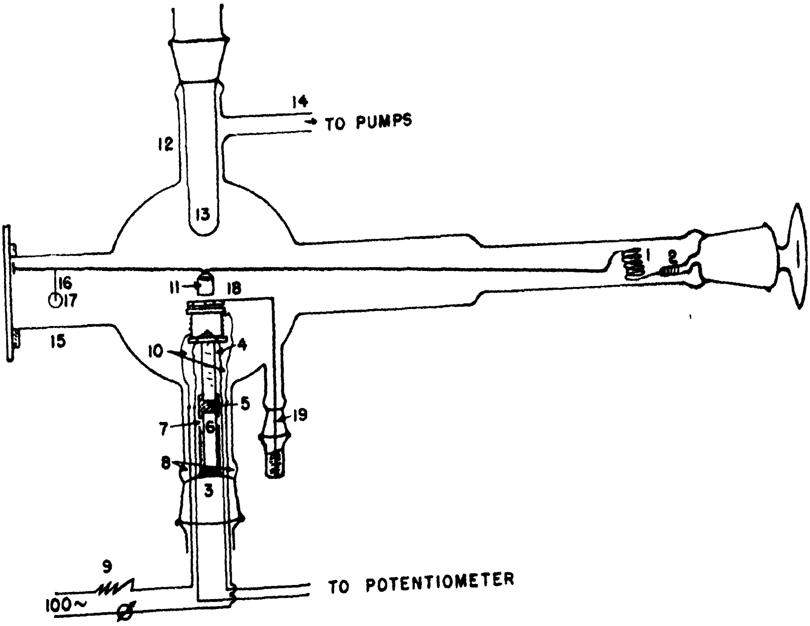


Fig. 1. Quartz spring balance apparatus.

The furnace is covered by a silvered glass disk (18) while being heated to the desired temperature. This lid is fixed to strong copper wire and the latter to a ground-glass joint (19). The vacuum is measured by a McLeod gage. Having attained the desired temperature, the silvered disk is rotated through an angle of about 60°, and the support (16) is lowered, so that the reaction vessel hangs freely inside the furnace. Before each run the outside of the reaction vessel is blackened with soot in order to adsorb the heat radiation efficiently.

Characteristics of Apparatus

The vacuum obtained in the apparatus is of the order of 10^{-5} to 10^{-6} mm. Hg. The temperature in the furnace can be kept constant within about ± 1°C. The thermocouple was calibrated in situ by introducing a calibrated thermocouple through the side tube (13) into the furnace, the apparatus being closed and evacuated.

The spring was calibrated by placing weights into the reaction vessel as follows:

Weight in reaction vessel	Division on scale in eyepiece of telescope
20 mg.	0
10 mg.	38
0 mg.	75

1 mg. ~ 3.75 divisions

This shows that Hooke's law is obeyed over this range of weights.

Next, the empty reaction vessel was placed on the beam in order to ascertain if any heat effects influence the measurements. The vessel was arrested, and the furnace covered by the silvered glass disk. The apparatus was evacuated, the furnace heated to 380°C., and the vessel lowered into it. An uncertainty, though small, arises at the beginning of the readings because the beam oscillates for two or three minutes, but the mean of the oscillations can be taken without difficulty. The results are given in Table I, which also shows the constancy of the temperature.

TABLE I. Blank Experiments (Empty Platinum Vessel). (1 mg. ~ 3.7 divisions)

t, min.	Divisions	Temperature, °C.	t, min.	Divisions	Temperature, °C.
0	23.5	391.0	14	22.5	381.5
1	23.5	388.5	19	22.0	380.0
2	23.0	386.0	23	22.0	381.5
3	23.5	383.5	27	22.0	381.5
5	23.0	381.5	33	22.0	381.5
7	23.0	380.0	42	22.0	381.5
9	23.0	381.5	60	22.0	381.5

Measurements were next carried out in which the vessel contained about 20 mg. polystyrene. The reaction vessel was weighed before and after the experiments. The number of divisions divided by the weight in milligrams of evaporated substance then gives the number of divisions per milligram. The mean of 19 experiments gave 3.7 divisions per milligram. Since half of one division can be estimated, the loss of weight can be ascertained to 0.14 mg.

The sensitivity of the instrument could be increased by fixing a mirror at the end of the quartz beam and observing the spot of light on a scale. This procedure of magnification is limited, however, by the magnitude of vibrations set up in the apparatus by outside influences.

Experimental Results

The experimental results are given in Figures 2-5, in which the percentage in grams of monomer produced (moles per base mole are obtained by dividing by 100) is plotted against the time in minutes. The unfractionated material, designated G ($\lim_{c\to 0} \eta/c = 8.4$), and 3 fractionated samples obtained from it ($F_V \lim_{c\to 0} \eta/c = 4.1$; $F_{III} \lim_{c\to 0} \eta/c = 9$; $F_{II} \lim_{c\to 0} \eta/c = 16$) were investigated.

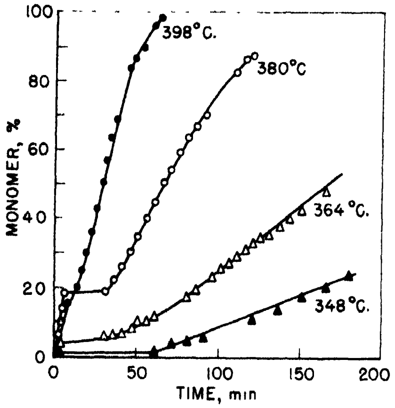


Fig. 2. Formation of monomer during degradation (fraction F_{II}).

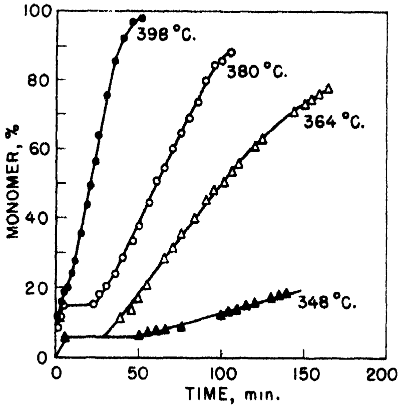


Fig. 3. Formation of monomer during degradation (fraction F_{III}).

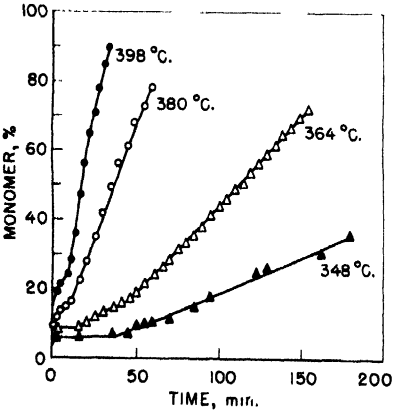


Fig. 4. Formation of monomer during degradation (fraction F_V).

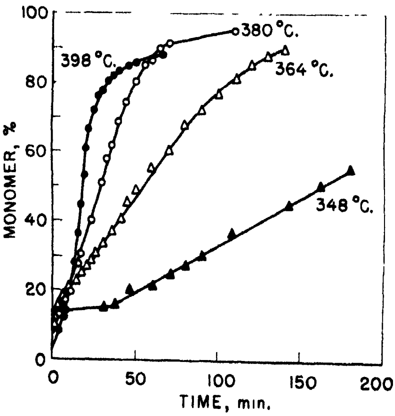


Fig. 5. Formation of monomer during degradation (unfractionated sample G).

All 4 samples give the same characteristic curves. A very rapid formation of monomer occurs at the beginning, and then slows down, giving rise to an apparent standstill of the reaction, which extends over half an hour at lower temperatures. The reaction becomes accelerated again following a straight-line course over a wide range; it finally slows down as the material becomes exhausted. That range of the reaction which follows a straight line — or, in other words, is of zero order — can be expressed as follows:

$$+\frac{dn}{dt} = k_{\text{exptl.}} \qquad (1)$$

(where n is the amount of monomer produced in grams and $k_{\text{exptl.}}$ is a rate constant) or in its integrated form:

$$n = k_{\text{exptl.}}t \qquad (2)$$

The experimental rate constants are given in Table II.

TABLE II. Rate Constants in Grams per Second (100 g. Initial Substance) and in Moles of Monomer Per Second Per Base Mole (Platinum Vessel)

Temp., °C.	G g./sec.	G mole/sec.	F_V g./sec.	F_V mole/sec.
398	6.6×10^{-2}	6.6×10^{-4}	4.84×10^{-2}	4.84×10^{-4}
380	2.82×10^{-2}	2.82×10^{-4}	2.14×10^{-2}	2.14×10^{-4}
364	1.10×10^{-2}	1.10×10^{-4}	8.31×10^{-3}	8.31×10^{-5}
348	4.56×10^{-3}	4.56×10^{-5}	3.47×10^{-3}	3.47×10^{-5}

Temp., °C.	F_{III} g./sec.	F_{III} mole/sec.	F_{II} g./sec.	F_{II} mole/sec.
398	4.07×10^{-2}	4.07×10^{-4}	3.47×10^{-2}	3.47×10^{-4}
380	1.72×10^{-2}	1.72×10^{-4}	1.59×10^{-2}	1.59×10^{-4}
364	6.6×10^{-3}	6.6×10^{-5}	6.02×10^{-3}	6.02×10^{-5}
348	2.88×10^{-3}	2.88×10^{-5}	3.16×10^{-3}	3.16×10^{-5}

Log $k_{exptl.}$ is plotted against 1/T in Figure 6 in order to obtain the energy of activation of the process. It is seen that the points for each fraction and the unfractionated material lie on parallel straight lines, the rates decreasing with increasing chain lengths of the fractions. The derived energy of activation amounts to -44.7 kcal. Equations of the form $k = A\ e^{-E/RT}$ g/sec. (initial material 100 g.) are set out below.
(k in mole/sec./base mole are obtained by dividing by 100).

G: $\lim_{c \to 0} \eta/c = 8.4$ $k_{exptl.} = 10^{13.30} \times e^{-44700/RT}$

F_V: $\lim_{c \to 0} \eta/c = 4.1$ $k_{exptl.} = 10^{13.19} \times e^{-44700/RT}$

F_{III}: $\lim_{c \to 0} \eta/c = 9.0$ $k_{exptl.} = 10^{13.12} \times e^{-44700/RT}$

F_{II}: $\lim_{c \to 0} \eta/c = 16.0$ $k_{exptl.} = 10^{13.05} \times e^{-44700/RT}$

Discussion of Experimental Results

A mechanism capable of accounting for the experimental results is that in which monomer units are split off successively from the chain ends. The number of chain ends will therefore be constant for a large part of the reaction. This mechanism was worked out by Simha, but a somewhat different and simplified derivation of our own will be given here. The assumption is that:

$$+\frac{dn}{dt} = -kg = \frac{dn_{mon}}{dt} \qquad (3)$$

where n ~ number of broken links, n_{mon} ~ number of monomer split off, and g ~ number of chain ends in the polymer sample.

The number of chain ends remains constant over a large part of the reaction; hence:

$$n_{mon} = n = kgt \qquad (4)$$

which yields a zero-order reaction, where kg = $k_{exptl.}$ The number of chains originally present is g/2. If s is the average number of broken links per chain, then:

$$g/2 \cdot s = n$$

hence:

$$g/2 \cdot s = kgt$$

or:

$$s = 2kt \qquad (5)$$

The number of broken links per chain is independent of the chain length for this mechanism.

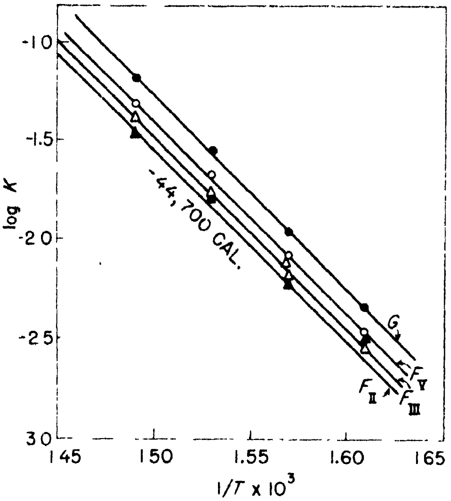


Fig. 6. Energy of activation for the process of formation of monomer from polystyrene.

The number-average chain length is, as always, given by:

$$P_n = \frac{P_0}{s + 1}$$

or, in this case:

$$P_n = \frac{P_0}{2kt + 1} \tag{6}$$

The expression for the weight-average chain length of the residual polymer will be approximately given by:

$$P_w \simeq P_0 - 2\,kt \simeq P_0 - s \tag{7}$$

If one deals with 1 base mole of monomer, or $1/P_0$ moles of polymer, equation 4 becomes:

$$n_{mon} = \frac{1}{P_0} 2\,kt \tag{8a}$$

hence:

$$k_{exptl.} = \frac{1}{P_0} 2\,k = gk \tag{8b}$$

One can thus find, with the help of equation 8b, the relative original chain length; or, if the chain length of one homogeneous sample is known (e.g., by osmotic measurements), one can find the degree of polymerization of another sample, since:

$$\frac{n_{mon_I}}{n_{mon_{II}}} = \frac{P_{0_{II}}}{P_{0_I}} = \frac{k_{exptl._I}}{k_{exptl._{II}}}$$

One can also determine the number-average chain length of an unfractionated sample by comparing its rate of monomer production with a fractionated sample of known chain length.

That the number-average chain length is involved, might be established through considerations which treat the same question from a somewhat different angle. Consider a chain of length b and one of length 2b. Then, assuming equal amounts in grams or base moles, b will have (2x2)/2 as many chain ends as 2b. Hence:

$$\frac{n_{mon,b}}{n_{mon,2b}} = \frac{kg_b t}{kg_{2b} t} = \frac{k_{exptl.,b}}{k_{exptl.,2b}} = 2\times 2/2$$

for b and 3b:

$$\frac{k_{exptl.,b}}{k_{exptl.,3b}} = \frac{2.3}{2}$$

for b and d (d > b):

$$\frac{k_{exptl.,b}}{k_{exptl.,d}} = \frac{2\frac{d}{b}}{2} = \frac{d}{b} \qquad (9)$$

If, for instance, d is known, b can be calculated. The determination of such a relative number-average chain length would proceed as follows. A fraction of the sample, as homogeneous as possible, would be prepared, and then its intrinsic viscosity determined. In the case of a fractionated sample, the weight-average chain length is equal (for all practical purposes) to the number-average chain length. Then, the rate constant for degradation of this fraction would be determined at a suitable temperature and also the rate constant for an equal amount in grams of the unfractionated material. The ratio of the two rate constants will be equal (to a good approximation) to the reciprocal ratio of the chain lengths (number-average for the unfractionated one) of the samples. If one does not know the actual chain length of the fractionated material, the result can be expressed in viscosity units: e.g., the intrinsic viscosity of the fraction may be "a" the ratio found, "c", and the number-average chain length in intrinsic viscosity units of the unfractionated material, "b". The number-average chain length of the fractionated material is then a/b = c times as large as the unfractionated one. The interpretation of the decrease in reaction velocity with increasing chain length can now be readily achieved. One must first examine the mechanism of degradation as a whole. The rapid degradation that takes place during the first few minutes is due to the breaking of weak links with subsequent splitting off of monomer units. Now, if one makes the reasonable assumption that the number of weak points in an original chain is proportional to its chain length, then, in samples of different chain length but of the same amount in grams (or base moles), there will be an equal number of weak links. Hence, if all the weak links are ruptured, as will be the case when the reaction slows down or begins to come into the range of zero order, a fractionated sample of definite chain length will then have 2x + 2 chain ends per original chain, where x is the number of weak links in the chain. Now, a fractionated sample of half the chain length, taking the same amount in grams, will have double the number of original chains, i.e., two chains for each chain of the previous one. The number of chain ends for the two small chains will therefore be 2x + 2 + 2; that is to say, in the second smaller fraction, there are:

$$\frac{2x + 2 + 2}{2x + 2} = \frac{x + 2}{x + 1}$$

as many chain ends as in the first one. If the ratio of the original chain lengths of two fractions is, say "b"/"d" (where "d" > "b"), one has:

$$\frac{x + \frac{d}{b}}{x + 1} = a$$

times as many chain ends in "b" as in "d" after breaking all weak links, x being the number of weak links in an original chain length "d".

For two fractions of chain lengths "d" and "b" ("d" > "b"), taking equal amounts, the following relationship exists:

$$a = \frac{x + d/b}{x + 1} = \frac{g_b}{g_d} = \frac{k_{\text{exptl.},b}}{k_{\text{exptl.},d}} \qquad (10)$$

This equation allows the calculation of the original number of weak links in the chain of length "d", although not, of course, in an accurate manner. Since it has been assumed that the number of weak links is proportional to the original chain length, the number of weak links for the original chains of the other fractions is also known. Table III shows the number of weak links for the fractions obtained in this way.

TABLE III

Fraction	$\lim_{c \to 0} \eta/c$	$\frac{g_V}{g_{II}} = 1.36$	$\frac{g_V}{g_{III}} = 1.19$	$\frac{g_{III}}{g_{II}} = 1.14$	From decrease of lim. visc.
F_V	4.1	1.84 ~ 2	2.46 ~ 2	1.14 ~ 1	3
F_{III}	9	4.1 ~ 4	5.4 ~ 5	2 6 ~ 3	5
F_{II}	16	7.2 ~ 7	9.6 ~ 10	4.6 ~ 5	9
F_I	24	— 11	— 15	— 8	15

The number of weak links assumed on the basis of the experiments on the decrease of the limiting viscosities are given for comparison, and agree quite well with those obtained by loss of weight measurements.

It may be observed in Figure 5 that unfractionated material G does not fall into line with the fractionated samples. G has an intrinsic viscosity of 8.4, and its log k vs. $^1/T$ curve should lie between F_V and F_{III}. This behavior can be explained partly as follows. As was shown above, the rate constants are governed by the number-average chain length (number of chain ends), but the intrinsic viscosity represents a weight-average chain length. The actual distribution of

G gives a ratio of $P_w/P_n = 1.68$, giving a number-average of about 5, which should cause the line for G to lie close to the one for F_V. However, there still remains a large discrepancy that cannot be explained satisfactorily at present. (It might be that there are some impurities accelerating the degradation present in the unfractionated material which are removed on fractionation.)

Decrease of Limiting Viscosity during Degradation at 363°C. in vacuo

A few experiments were performed at 363°C. in vacuo using F_{III} to see if the decrease in the limiting viscosity is in accordance with the mechanism proposed here. These experiments were carried out by interrupting the degradation at various stages and measuring the limiting viscosities of the samples.

One would expect, according to equation 7, a straight-line relationship between the intrinsic viscosities and time starting with a homogeneous sample. The present case is somewhat more complicated, since, at the beginning of the reaction, degradation is caused by the rupture of the chains at the weak points, and the material is no longer homogeneous once the splitting off of the monomer starts. Nevertheless, a straight-line relationship is obtained, as Figure 7 shows. The values obtained are given in Table IV.

TABLE IV. Decrease of Limiting Viscosities at 363° C. in vacuo for F_{III}

t, min.	Loss, gram per cent	$\lim_{c \to 0} \eta/c$	P
0	0	9.1	1140
10	3.5	5.75	720
22	4.2	5.90	690
30	8.9	4.6	575
60	24	4.0	500
90	32.6	3.3	412

The rate constant for the reaction can be obtained using equation 7. The limiting viscosities were converted into chain lengths by using the same Staudinger constant, 8×10^{-3}, as Part I. A value of $k = 2.26 \times 10^{-2}$ $sec.^{-1}$ was found, which gives $P_0 = 590$, a value very close to that obtained at the end of the induction period.

By using equation 8b, $k_{exptl.}$ can be calculated. A value of $k_{exptl.} = 7.66 \times 10^{-5}$ mole/sec./base mole obtained in this way compares favorably with the constant found from the previous loss-of-weight experiments at this temperature: $K_{exptl.} = 6.6 \times 10^{-5}$ mole/sec./base mole.

It is opportune to discuss at this point a paper by Kobeko (2) and co-workers. These authors present a theoretical derivation of distributions obtained by degradation of a sample possessing a definite initial distribution, assuming random breaking of links. From the distribution functions derived in this way they also obtain the expression for the amount of monomer produced during degradation, and, from this, an expression for the percentage U of material not degraded to the monomer. The values obtained theoretically for U agree quite well with those obtained experimentally. Polymethyl methacrylate and polystyrene ($P_0 = 4000$) were investigated, the latter under nitrogen and in the presence of atmospheric oxygen.

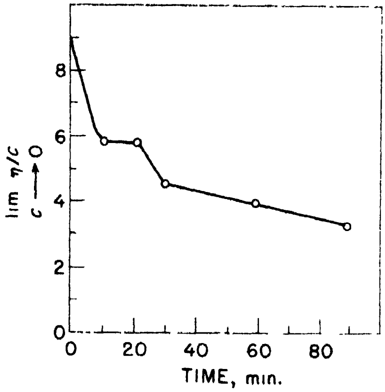


Fig. 7. Decrease of limiting viscosity of fraction F_{III} during degradation at 363°C in vacuo.

The experimental technique employed in the presence of nitrogen-great care was taken to exclude oxygen-consisted in placing 300 to 400 g. finely crushed substance in a retort, condensing the monomer vapor, and collecting it in a cylindrical measure. This method seems to be rather crude compared with that employed in this work.

The value given by these workers for the energy of activation, derived from 3 experiments in an atmosphere of nitrogen (300, 375, and 400°C.), is -34,000 cal; in air (200, 250, and 300°C.), -10,000 cals.

Unfortunately, these authors did not carry out any viscosity measurements, or they would have noticed that the theory of random breaking of links is not at all compatible with the experimental results. An example may illustrate this: A sample of chain length P_0 = 1000 may be degraded to such an extent that the amount of monomer produced is 25% of the original material. This corresponds to a degree of degradation (alpha) of 0.5, according to the random theory of breaking links. Table V shows the weight distribution for this case.

It clearly follows that the average chain length of the residual material cannot be larger than 10. This result will now be compared with those obtained experimentally. In Table IV, the decrease of the limiting viscosities and the simultaneous loss in weight were given for sample F_{III} at 363°C. in vacuo. The initial viscosity is 9.1, corresponding to an initial chain length of $P_0 = 1140$. After 60 minutes, 25% of the original material is transformed into monomer, but the limiting viscosity of the residual material is 4.0, or its chain length, 500. These results show very clearly indeed how incompatible the theory of random breaking is with the experimental results.

The two experimental runs at 375° and 400° carried out in nitrogen by Kobeko and co-workers (2) actually, give when evaluated in the manner described in this work, an energy of activation of about -40 kcal., which is in reasonable agreement with the value of -44.7 kcal. obtained by our method.

TABLE V. Distribution of Chain Lengths when P_o = 1000, α = 0.5. 1 g. Initial Material; m_p = Weight, in Grams of Chains of Length P

P	m_p
500	3.8×10^{-149}
100	1.8×10^{-29}
20	1.0×10^{-5}
10	4.8×10^{-2}
5	7.9×10^{-2}
2	2.5×10^{-1}
1	2.5×10^{-1}

Influence of Platinum Surface on Degradation

A few comparative runs were carried out in a Pyrex and platinum reaction vessel at 312°C. in order to find out if the platinum surface influences the degradation.

As Table VI shows, there is a marked effect - the reaction being slowed down in the platinum vessel.

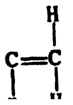
TABLE VI. Loss of Weight and Decrease of Limiting Viscosity in Pyrex Glass and Platinum Vessels at 312°C. for G. (Initial substance about 20 mg.)

t, min.	Weight loss, gram per cent		Limiting viscosity	
	Pyrex	Pt	Pyrex	Pt
0	0	0	8.4	8.4
30	4.1	2.9	6.6	6.5
60	6.4	2.6	5.5	6.4
100	7.6	4.6	5.1	6.5

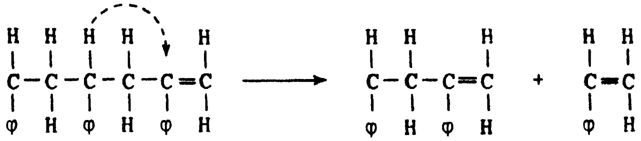
This behavior can be accounted for by assuming that the reaction, which leads to a decomposition of the oxygen groups without rupturing the polymer chains, is catalytically favored at a Pt surface.

Elementary Steps

The chain ends present in the material are the original chain ends and those produced by rupturing chains at the weak points. We do not know the nature of the end groups in polystyrene but it is not unlikely that either double bonds or methyl groups are present at the end of a polystyrene chain. The end of a chain produced by rupture at a weak point and subsequent splitting off of monomer units has, according to the mechanism proposed in Part I, a double bond. Thus one has mainly to deal with end groups as follows:



These will become activated, the reaction leading to the formation of a monomer unit:



Conclusions

The mechanism suggested accounts satisfactorily for the apparent zero order of the reaction, the dependence of the rate of degradation on the chain length, and the dependence of the decrease of the limiting viscosity on time. It allows the number of weak points in a chain to be estimated, these estimated numbers comparing favorably with those assumed on the basis of the experiments discussed in Part I. The influence of the Pt surface on degradation can be considered as another argument in favor of the assumption that oxygen groups are present in the polystyrene chain.

DEGRADATION OF POLY-ALPHA-METHYLSTYRENE IN VACUO

A sample of poly-alpha-methylstyrene of about 70,000 molecular weight was degraded in the apparatus described above in order to investigate the influence the methyl group exerts on the stability of the polymer. The amounts of substance employed in each experiment were about 20 mg. It was observed at once that the rate of production of monomer is very much faster than the rate for the ordinary polystyrene. The experimental curves are presented in Figure 8, where the percentage of monomer produced is plotted against the time in minutes. The experiments were carried out over a range of temperatures from 280° to 363°C. It will be observed that the curves show characteristic differences from those of polystyrene. They show a linear portion up to about 30% monomer production, varying somewhat with temperature; the reaction then slows down, and is accelerated in its later stages, - only one of the curves showing an exception.

Rate constants have been derived for the initial straight portion of the curves, or, in other words, the range for which the reaction seems to be apparent of zero order. These constants are given in Table VII.

The energy of activation can be obtained for this range of temperatures by plotting log K values against 1/T (Fig. 9). Since the rate constants stray somewhat, the straight line has been drawn by the method of least squares. The point for the lowest temperature (281°) seems particularly far off the line; since it was observed that near this temperature the substance goes into the fluid state, this point

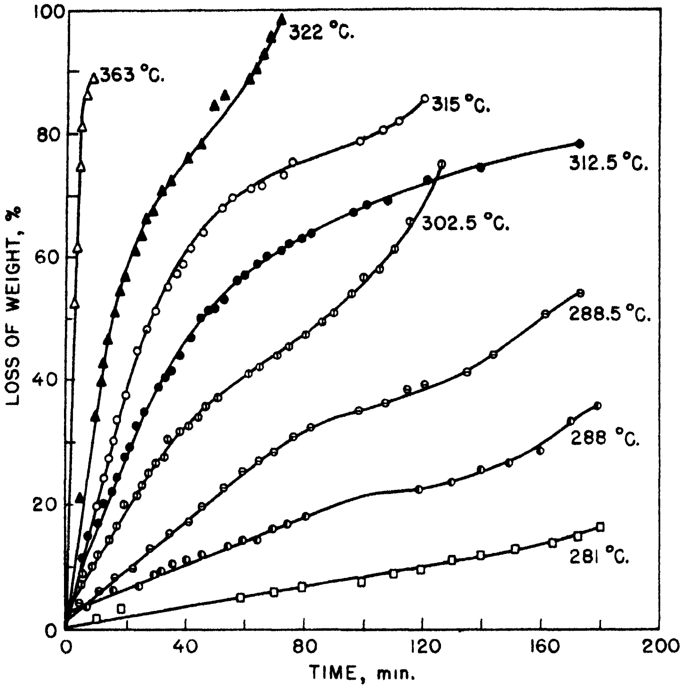


Fig. 8. Degradation of poly-alpha-methylstyrene in vacuo.

could not be considered reliable and was therefore excluded from the calculations. The energy of activation found for the process amounts to -45.1 kcal., and the initial reaction is given by an Arrhenius equation as follows:

$$K = 1.58 \times 10^{15}\ e^{-45100/RT}\ \text{sec.}^{-1}\ (\text{g./100 g.})$$

This energy of activation is very similar to that found for poly-

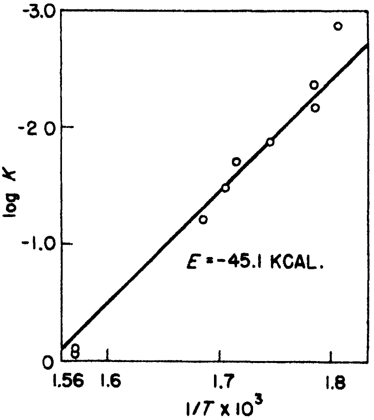


Fig. 9. Energy of activation for the degradation of poly-alpha-methylstyrene.

styrene (-44.7 cal.); the higher rate of degradation is due to the higher A factor. Since the rate constants stray somewhat, it is difficult to decide if this difference in the A factor is significant; an energy of activation of about 5% less than that given above would give an A factor of the same magnitude as the one for polystyrene (10^{13}). Moreover, all the rate constants contain the number of chain ends in the system, that is, they are dependent on chain length, and, if poly-alpha-methylstyrene may be assumed to be branched, on the number of these branches.

TABLE VII Degradation of Poly-alpha-methylstyrene in vacuo

Temperature, °C.	K, g./sec /100 g.	K, mole/sec./base mole
363	0.795	7.95×10^{-3}
363	0.884	8.84×10^{-3}
322	0.619	6.19×10^{-4}
315	0.0334	3.34×10^{-4}
312.5	0.0198	1.98×10^{-4}
302.5	0.0132	1.32×10^{-4}
288.5	0.00655	6.55×10^{-5}
288	0.00339	3.39×10^{-5}
281	0.00139	1.39×10^{-5}

It is difficult to say anything definite about the mechanism of the reaction. The initial part of the reaction, yielding straight lines up to about 30%, can be accounted for by assuming that monomer breaks off the chain ends in a manner similar to that found for polystyrene. The slowing down of the reaction can either be due to using up of the branches or to inhibitors. There is also a possibility that the slowing down is due to some kind of net structure of the polymer, the more mobile chain ends being used up first. The peculiar acceleration of the reaction in its later stages does not seem to be compatible with a mere using up of branches; the reaction should in that case go on at a reduced speed and give a straight line. This may be illustrated by a brief discussion of the degradation of a branched chain.

Degradation of a Branched Chain

The chain length of the main chain is P_0, and that of the branches, P'_0. Each chain has, on the average, "a" branches. Monomers are split off successively from the main chain ends and from the branch ends.

During the first stages of the degradation, the total amount of the chain ends may be considered constant. One has:

$$^{dn}/_{dt} = -kg$$

$$n = -kgt$$

if m_0 = number of main chains at t = 0, then:

$$sm_0 = ktm_0(2+a)$$

where s = number of links ruptured on the average per original chain. Hence:

$$s = kt(2+a)$$

Starting with one base mole of polymer or $1/(P_0 + aP'_0)$ moles of polymer, one has:

$$n_{mon} = \frac{1}{P_0 + aP'_0} \times s = \frac{2+a}{P_0 + aP'_0} \times kt \qquad (11)$$

As soon as the branches are used up the rate of monomer production will fall off, and equation 11 becomes:

$$n_{mon} = \frac{2}{P_0 + aP'_0} kt$$

An example may illustrate this. We have a polymer with characteristics as follows: $P_0 = 600$; $P'_0 = 30$; and a = 10. The initial rate constant may be 1.32×10^{-4} mole/sec./base mole. Then:

$$K_{exptl.} = \frac{2+a}{P_0 + aP'_0} \times K = 1.32 \times 10^{-4} \text{sec.}^{-1}$$

After about 33% (Fig. 10) of the material has been transformed into monomer, the branches will be used up, and the rate constant will be given by:

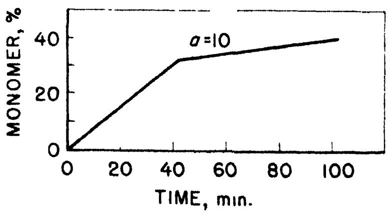


Fig. 10. Degradation of a branched polymer.

$$K_{exptl.} = \frac{2}{P_0 + aP'_0} \times K = 2.2 \times 10^{-5} \text{sec.}^{-1}$$

DEGRADATION OF CROSS LINKED POLYSTYRENE IN VACUO AT 364°C.

A number of experiments were performed in order to study the effect of cross links on degradation.

The samples were polystyrenes polymerized in the presence of various amounts of m-divinylbenzene. Some were polymerized in the presence of benzoyl peroxide. The samples were first dried in high vacuum at about 200°C. for 30 to 60 minutes to remove the residual monomer (about 5%). The experimental results are given in Figure 11, where, again, the percentage of monomer produced is plotted against the time in minutes.

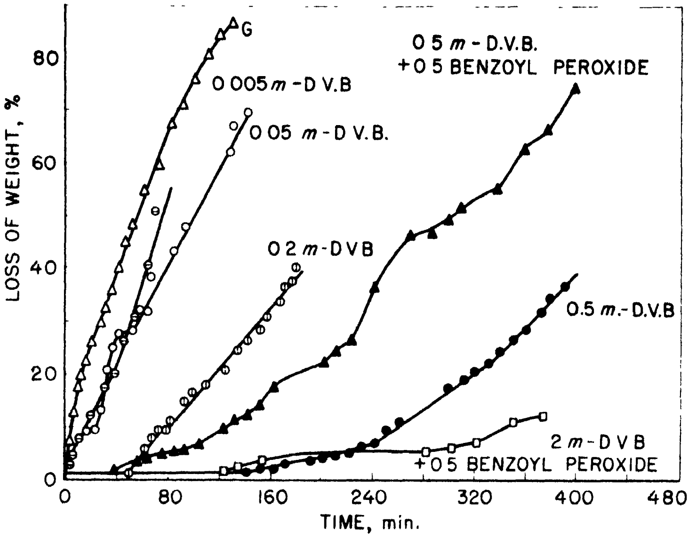


Fig. 11. Degradation of cross-linked polystyrene (m-divinylbenzene) in vacuo.

The samples containing 0.5 and 0.2% m-divinylbenzene have very long induction periods (140 and 44 minutes, respectively); during this induction period the substance does not melt, but at the end of this time interval it begins to sinter and eventually melts. This behavior gives the impression that the net structure of the polymer has to be broken down first, and, that when this is achieved, the polymer goes over into the fluid state, the chain ends then having sufficient thermal mobility to split off monomers. The samples with lower content of m-divinylbenzene (0.05 and 0.005%) already melt below 200°C. and show only short induction periods. Samples polymerized in the presence of benzoyl peroxide as catalyst are not as stable as the corresponding samples prepared without catalyst. The induction period is considerably shortened (34 minutes, compared with 140 minutes for the 0.5% m-divinylbenzene). It is premature to attempt any explanation for the instability of the catalyzed polymerizates, but it may well be that peroxide fragments which facilitate the breakdown of the net structure are incorporated into the polymer. The rate constants for the samples derived from the part of the reaction that is of zero order are comprised in Table VIII.

It might be possible to characterize cross-linked polystyrene by means of the induction period, the latter being a function of the percentage of m-divinylbenzene present. By studying one specific sample at different temperatures, the energy of activation for breaking cross links could be obtained. It is reasonable to assume that almost all the cross links are broken at the end of the induction period. If at a temperature T_1 an induction period of t_1 minutes is observed, and, at T_2, one of t_2 minutes, then:

TABLE VIII Rate Constants of Cross-linked Polystyrene Polymerized in the Presence of m-Divinylbenzene. Data Derived from using Zero-Order Part of Reaction at 364° C. in vacuo Using Platinum Vessel

Conc., of meta-D.V.B., %	K, g./100 g./sec.	K, g./base mole/sec.
0.005	1.35×10^{-2}	1.3×10^{-4}
0.05	7.57×10^{-3}	7.27×10^{-5}
0.2	4.82×10^{-5}	$4\ 63 \times 10^{-7}$
0.5	3.16×10^{-5}	3.04×10^{-7}

$$t_1/t_2 = k_2/k_1$$

where k_1 and k_2 are the relevant reaction-rate constants for breaking cross links. The energy of activation for the process can then be derived by plotting log k against 1/T.

DEGRADATION OF POLYETHYLENE IN VACUO

Samples of polyethylene were also degraded in the apparatus described above, the main object being to ascertain the energy of activation for the process. It was thought that a comparison of the energy of activation with the values obtained for polystyrene might throw some light on the influence of different substituents in the polymer chain on the stability of the C-C links.

The samples were unfractionated and had different average molecular weights. They contained 0.1% Monoxol (grade 2 ~ average molecular weight 23,000; grade 20 ~ average molecular weight, 16,000; grade 200 ~ average molecular weight 11,000).

To get the polymer in the molten state, the samples were kept at about 200°C. for one hour in vacuo before being heated to temperatures at which degradation occurs.

The experimental results are shown in Figures 12-14 where, again, the percentage of evaporated substance is plotted against the time in minutes. It is seen that the curves are linear over quite a considerable range of the degradation, the reaction slowing down in the later stages. Some of the curves show rapid degradation in the very beginning of the reaction, as in the case of polystyrene, but, since no viscosity measurements have been carried out, comment as to the nature of this rapid degradation cannot be made.

The results show that polythene is more heat resistant than polystyrene and poly-alpha-methylstyrene, which is to be expected because the presence of phenyl and methyl groups in the chain will weaken the

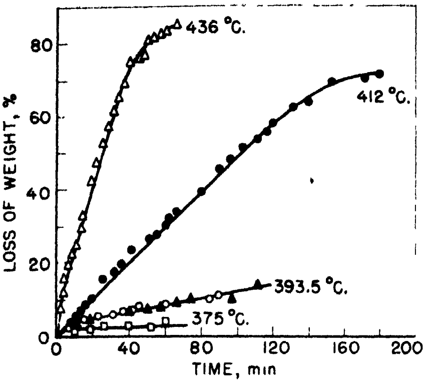


Fig. 12. Degradation of polythene, Grade 2, average molecular weight 23,000

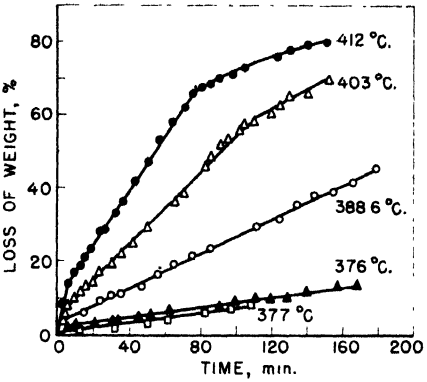


Fig. 13. Degradation of polythene, Grade 20, average molecular weight 16,000

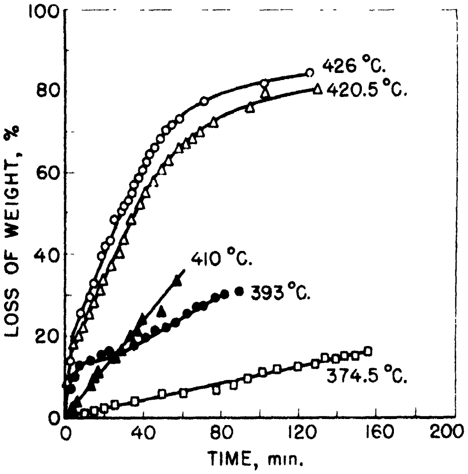


Fig. 14. Degradation of polythene, Grade 200, average molecular weight 11,000.

the C-C links. The rate constants for the part of the degradation that is of zero order for the various samples and temperatures is given in Table IX.

The energy of activation for the process was obtained by plotting log k against 1/T (Fig. 15). One significant difference from polystyrene emerges clearly: the energy of activation of polyethylene is dependent on chain length, decreasing with decreasing chain length:

Grade	Av. mol. wt.	E, kcal.
2	23,000	66.1
20	16,000	52.6
200	11,000	46.0

The energy of activation for polystyrene is 44.7 kcal. and is independent of chain length.

TABLE IX. Degradation of Polythene ("Alkathene") in vacuo

Temperature, °C.	K, g./100 g./ sec.
Grade 2 (mol. wt. 23,000)	
436	0.0304
412	0.0080
393.4	0.00153
375	0.00018
Grade 20 (mol. wt. 16,000)	
412	0.0124
403	0.0081
388.6	0.0039
377	0.0013
376	0.0012
Grade 200 (mol. wt. 11,000)	
426	0.0208
420.5	0.0169
410	0.0097
393	0.0045
374.5	0 0017

The rate constants (in g./100/sec.) can be represented by Arrhenius equations as follows:

$$\text{Grade 2} \quad K_2 = 10^{18.8} e^{-66100/RT}$$

$$\text{Grade 20} \quad K_{20} = 10^{14.8} e^{-52600/RT}$$

$$\text{Grade 200} \quad K_{200} = 10^{12.64} e^{-46000/RT}$$

Multiplying by the average initial chain length P_0, and dividing by 100, one obtains (in moles per mole polymer per second):

$$P_0 \; 822 \quad K_2 = 5.2 \times 10^{19} e^{-66100/RT}$$

$$P_0 \; 571 \quad K_{20} = 3.6 \times 10^{15} e^{-52600/RT}$$

$$P_0 \; 393 \quad K_{200} = 1.6 \times 10^{13} e^{-46000/RT}$$

It is also of interest to express the rate constants by the statistical expression:

$$K' = \frac{kT}{h} e^{\Delta S/R} \; e^{-\Delta H/RT}$$

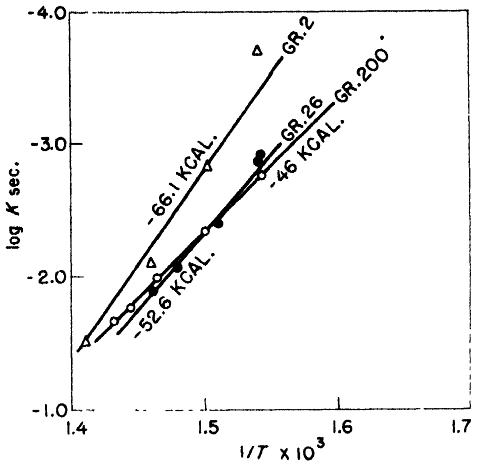


Fig. 15. Energies of activation for the degradation of polyethylene.

The entropies of activation obtained in this way are as follows:

Grade	$e^{\Delta S/R}$	ΔS, cal./degree
2	3.7×10^6	+30.2
20	2.6×10^2	+11.1
200	1.1	+ 2.3

The term $e^{\Delta S/R}$ corresponds to the probability factor P in the Arrhenius equation.

It is clear that the theory of random breaking is not applicable to the degradation of polyethylene, since, for instance, the residue still consists of polymer after a loss of weight of 40%. But the mechanism by which monomer breaks off, one segment after another, from the chain ends also seems incompatible with the experimental results.

A mechanism that could account for the observed experimental results is one in which the first or last monomer unit is broken off the chain; as soon as this has happened, the whole chain degrades completely by breaking off monomer units in rapid succession. The kinetics of such a mechanism is, briefly, as follows. The rate of decrease of chain ends is:

$$-dg/dt = kg$$

hence:

$$g = g_0 e^{-kt}$$

or:

$$\ln(g/g_0) = -kt$$

since:

$$P_0 \frac{g_0 - g}{2} = n_{mon}$$

or:

$$g = g_0 - \frac{2n_{mon}}{P_0}$$

one obtains:

$$\ln\left(1 - \frac{2n_{mon}}{g_0 P_0}\right) = -kt$$

For one mole of polymer, or 2 moles of chain ends, the expression becomes:

$$\ln\left(1 - \frac{n_{mon}}{P_0}\right) = -kt \qquad (12)$$

The experimental results have been evaluated according to equation 12, straight lines being obtained by plotting log (1 - $[n_{mon}/P_o]$) against t in minutes. The energies of activation are the same as those obtained before. The rate constants (per second) given by the Arrhenius equations are:

Grade 2 P_0 822 $K_2 = 6.65 \times 10^{13} e^{-66000/RT}$

Grade 20 P_0 571 $K_{20} = 1.18 \times 10^{10} e^{-52600/RT}$

Grade 200 P_0 393 $K_{200} = 8.35 \times 10^{7} e^{-45600/RT}$

The mechanism outlined above represents well the experimental data and removes the difficulty arising from the dependence of the energy of activation on chain length. But viscosity measurements at various stages during the degradation will have to decide the correctness of the proposed mechanism.

Acknowledgment

It is the author's great pleasure to thank Prof. E. K. Rideal F.R.S. for advice and helpful discussions; he also wishes to express his thanks to the Distillers Company Ltd. for financial assistance. Parts I-III were completed during the years of 1942-1945.

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Synopsis

An apparatus has been constructed which enables one to follow continuously the formation of monomer during degradation in vacuum. Experimental results are presented on the degradation of fractionated and unfractionated polystyrene over a range of temperatures from 340-400°C. in vacuum. A mechanism has been proposed which accounts satisfactorily for the apparent zero-order reaction and for the dependence of the rate of degradation on chain length. This mechanism allows one to estimate relative number average molecular weights and the number of weak points per original chain. The influence of a platinum surface on degradation has been indicated. The degradation of poly-alpha-methylstyrene has been investigated over a range of temperatures from 281 to 363°C. in vacuum. The mechanism of the degradation of branched polymer chains has been discussed. The degradation of cross-linked polystyrene containing various amount of m-divinylbenzene has been studied at 364°C. in vacuum. The reaction shows long induction periods depending on the amount of m-divinylbenzene and on the presence of benzoyl peroxide during polymerization. The degradation of polyethylene shows this polymer to be more heat resistant than polystyrene. Various grades of different average molecular weight have been investigated over a range of temperatures from 375 to 436°C. in vacuum. The energy of activation has been found dependent on chain length. A mechanism has been suggested to account for the observed experimental results.

Résumé

Un appareil permettant de suivre de façon continue la formation de monomère au cours de la dégradation a été construit. Les résultats expérimentaux se rapportent à la dégradation d'échantillons de polystyrols fractionnés et bruts dans un intervalle de témperature de 340° à 400° C. sous vide. Un mécanisme est présenté, en accord avec une réaction d'un ordre apparent zéro, et en accord avec la dépendance de la vitesse de dégradation des longueurs de chaîne. Ce mécanisme permet l'évaluation des répartitions des poids moléculaires, et du nombre de points faibles dans chaque chaîne initiale. L'influence d'une surface de platine sur la dégradation est indiquée. La dégradation du poly-alpha-methylstyrol a été étudiée sous vide sur un intervalle de température de 281 à 363°C.; le mécanisme de dégradation de polymèrs ramifiés est discuté. La dégradation du polystyrol, ponté ("cross linked") par des quantités variables de m-divinylbenzene, a été étudiée à 364°C. sous vide. La réaction présente de longues périodes d'induction, qui sont fonction, à la fois, de la quantité de m-divinylbenzene présent, et de la présence de peroxyde de benzoyle durant la polymérisation. La dégradation du polyéthylène manifeste une résistance thermique plus élevée que celle du polystyrol. Des échantillons de différents poids moléculaires ont été étudiés sous vide dans un intervalle de témperature de 375 à 436°C. L'énergie d'activation est fonction de la longueur de chaîne. Un mécanisme est suggéré pour interpréter les résultats expérimentaux obtenus.

Zusammenfassung

Es wird eine Apparatur entwickelt, die die kontinuierliche Verfolgung der Bildung von Monomeren während Abbaureaktionen im Vakuum ermöglicht. Experimentelle Resultate werden gegeben für den Abbau von fraktioniertem und nicht-fraktioniertem Polystyrol über ein Temperaturberreich von 340 bis 400°C. im Vakuum. Es wird ein Mechanismus vorgeschlagen, der die scheinbare 0-te Order-Reaktion hinreichend erklärt und der die Abhängigkeit des Abbaugrades von der Kettenlänge erklärt. Dieser Mechanismus gestattet, das relative Zahlendurchschnittsmolekulargewicht und die Zahl der schwachen Punkte der Originalkette zu berechnen. Der Einfluss einer Platinoberfläche auf den Abbau wird gezeigt. Es wird der Abbau von Poly-alpha-methylstyrol über ein Temperaturbereich von 281° bis 363° im Vakuum untersucht. Es wird der Mechanismus des Abbaues von verzweigten Polymerketten diskutiert. Der Abbau von vernetzten Poly-

styrolen, die einen variierenden Betrag von Metadivinylbenzol enthalten, wird bei 364°C. im Vakuum studiert. Diese Reaktion zeigt eine lange Induktionsperiode, die von dem Betrag des vorhandenen Metadivinylbenzols und von der Gegenwart von Benzoylperoxyd während der Polymerisation bestimmt wird. Der Abbau von Polyäthylen zeigt, dass dieses Polymer hitzebeständiger als Polystyrol ist. Es werden verschiedene Proben von verschiedenem Durchschnitts-Molekulargewicht über ein Temperaturbereich von 375° bis 436° im Vakuum untersucht. Es wird gefunden, dass die Aktivierungsenergie von der Kettenlänge abhängig ist. Es wird ein Reaktionsmechanismus vorgeschlagen, der die Experimente erklärt.

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Application of Infrared Anaylsis to Elucidate the Mechanism of the Boron Trifluoride Catalyzed Vapor Phase Polymerization of Isobutene at Room Temperature

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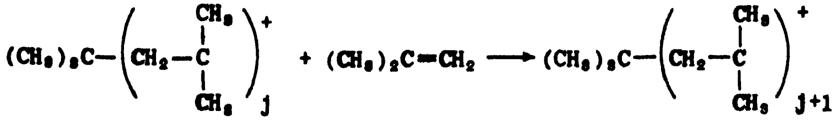
The polymerization of isobutene gas catalyzed by boron trifluoride (BF_3) at room temperatures probably proceeds by a mechanism closely related to that of the low-temperature reaction catalyzed by Friedel-Craft type catalysts, such as BF_3, $SnCl_4$, $AlCl_3$, etc. Both reactions require a cocatalyst and Evans, Meadows, and Polanyi (1) have shown that the vapor-phase reaction at room temperature is heterogeneous, occurring at the surface of crystallites of the BF_3-cocatalyst complex. Several modes of action of the catalyst can be postulated (2), but the most likely, in view of the fact that the cocatalyst (denoted by ROH) usually contains a hydroxyl group, is that proposed by Polanyi and others (3), in which the initiation step is the surrender of a proton by the complex (written as $BF_3.ROH$) to a molecule of isobutene. Since the stability of carbonium ions increases with the number of alkyl groups that are attached to the positively charged carbon atom (4) the more likely of the two modes of addition (equation 1a and 1b below) is that resulting in the formation of the trimethyl carbonium ion, i.e., reaction 1a.

$$BF_3.ROH + (CH_3)_2C{=}CH_2 \longrightarrow BF_3.RO^- + (CH_3)_3C^+ \qquad (1a)$$

or

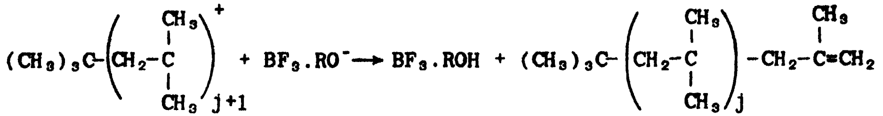
$$+ (CH_3)_2CH{-}CH_2^+ \qquad (1b)$$

The finished polymer is known to have a head-to-tail structure, and if we assume the cation of equation 1a to be the initiating center, the propagation reaction is written as the charge transfer process:

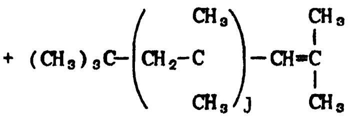


$$(CH_3)_3C{-}\left(CH_2{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\right)_j^+ + (CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_3C{-}\left(CH_2{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\right)_{j+1}^+ \qquad (2)$$

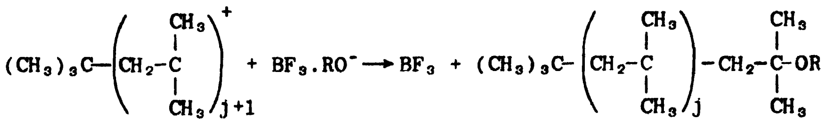
Termination of such reaction chains requires charge neutralization and therefore involves the anionic fragment ($BF_3.RO^-$) of the complex. It may occur either by proton expulsion from the growing chain, as in equations 3a and 3b, or by addition of the anionic fragment of the cocatalyst (RO^-) as in reaction 4.



$$(CH_3)_3C\text{-}\left(CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}\right)^{+}_{j+1} + BF_3.RO^- \longrightarrow BF_3.ROH + (CH_3)_3C\text{-}\left(CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}\right)_{j}\text{-}CH_2\text{-}\overset{CH_3}{C}{=}CH_2 \quad (3a)$$

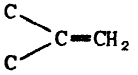


$$+\ (CH_3)_3C\text{-}\left(CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}\right)_{j}\text{-}CH{=}\overset{CH_3}{\underset{CH_3}{C}} \quad (3b)$$



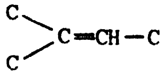
$$(CH_3)_3C\text{—}\left(CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}\right)^{+}_{j+1} + BF_3.RO^- \longrightarrow BF_3 + (CH_3)_3C\text{-}\left(CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}\right)_{j}\text{-}CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}OR \quad (4)$$

If the initiation reaction is equation 1a the finished polymer should contain the end group $(CH_3)_3C$-. Further, if proton expulsion is the termination process the polymer will contain an olefinic linkage, which will be either:



$$\begin{matrix}C\\ C\end{matrix}\!\!>C{=}CH_2$$

(3a) or



$$\begin{matrix}C\\ C\end{matrix}\!\!>C{=}CH\text{—}C$$

(3b)

depending on whether the expulsion takes place from a methyl ($-CH_3$) or methylene ($-CH_2$) group. On the other hand, if reaction 4 is occurring, the final polymer will not be unsaturated and will contain the C-O-R group. Determination of the structure of the end groups will therefore provide unambiguous evidence concerning the reaction mechanism. Moreover, if the cocatalyst is deuterated, the evidence can be extended. For example, if D_2O is used as cocatalyst, the polymer should contain the end groups $-CH_2D$, corresponding to reaction 1a, or $(CH_3)_2\dot{C}D$, corresponding to reaction 1b. If reaction 4 is the termination step the C-O-D group will be present but no H_2O or HOD will be formed, whereas, if reaction 3a or 3b occur to the exclusion of reaction 4, the C-O-D group will be absent and the cocatalyst may be expected to change progressively as the reaction proceeds from $D_2O \rightarrow HOD \rightarrow H_2O$.

Although chemical tests for unsaturation might reveal the presence of an olefinic linkage in the polymer, the complete characterization of this and other linkages by chemical means would be both tedious and uncertain. It therefore seemed preferable to employ a rapid physical method, namely, the measurement of the infrared absorption spectrum of the polymer and catalyst-cocatalyst complex in the wave length range of 2-14 μ. To obtain relatively strong absorption by the end groups it is desirable to use polymers of as low a chain length as possible. The polymer from the vapor phase reaction at room temperature, which can be made with an average degree of polymerization of about 10, was therefore employed. The fact that this polymer is a liquid is also advantageous.

The infrared spectra of pure liquid hydrocarbons of molecular formulas $(C_4H_8)_3$ and $(C_4H_8)_4$ have been measured by Kletz and Price (5) and used by these authors to establish the structural formulas. While such compounds may be regarded formally as trimer and tetramer respectively, of butene, they are not prepared from polymerizations of isobutene, but the $(C_4H_8)_4$ is formed from the dimerization of di-isobutene ($(CH_3)_3C\text{-}CH_2\text{-}C(\text{-}CH_3){=}CH_2$), and the $(C_4H_8)_3$ is said to arise from a dismutation reaction between $(C_4H_8)_2$ and $(C_4H_8)_4$. Steric hindrance prevents di-isobutene from polymerization beyond the dimeric stage. These tri- and tetramers of butene do not contain the head-to-tail structure characteristic of the products of polymerization of isobutene. Furthermore the vapor pressure of these products would probably have been measurable at the temperature of our experiments (6), whereas our products had no detectable vapor pressure. We therefore conclude that the dodecene and hexadecene studied by these authors are not present in our polymer.

PREPARATION OF THE POLYMER

23 mm. of BF_3 gas was condensed from a given volume into a spherical Pyrex reaction vessel of about 100-ml. capacity provided with a draining tube. 5 mm. of D_2O vapor was condensed from the same space into the same vessel. The low-temperature bath was then removed and the vessel allowed to warm up to room temperature (26°C.). Pure, dry isobutene gas was then allowed to leak continuously into the reaction vessel, to an extent corresponding to a pressure of about 2500 mm. During this operation droplets of polymer appeared, grew, and sometimes coalesced on the vessel walls, and then drained into the sump. Some of the catalyst-cocatalyst complex was carried down with the polymer, giving rise to some turbidity, much of which cleared on standing. This product had no detectable vapor pressure, but was nevertheless pumped out at room temperature, for several hours, to remove all possible traces of any monomeric isobutene, before being used for analysis. (We are greatly indebted to Mr. K. E. Russell for supplying the isobutene and BF_3 gases and for considerable help.)

MEASUREMENT OF THE SPECTRA

The spectra shown in Figure 1 were obtained on a Standard Perkin Elmer Model 12B infrared spectrometer fitted with a rock-salt prism. A layer of liquid polymer 0.076-mm. thick was suitable for the majority of the bands between 7 and 14 μ (B). At shorter wave lengths, two other thicknesses were used to bring out bands of varying intensity, the thicker layer (A) being 0.70 mm., the thinner one (C) being a capillary layer of the order of 0.01 mm. (We are grateful to Mr. H. C. Wheately for running the spectra.)

DISCUSSION

In the spectrum of polyisobutene samples of high average molecular weight, bands due to the end groups are normally unobservable. In the spectrum of the low-molecular polymer considered here, the end groups should give bands of comparable intensity to those arising

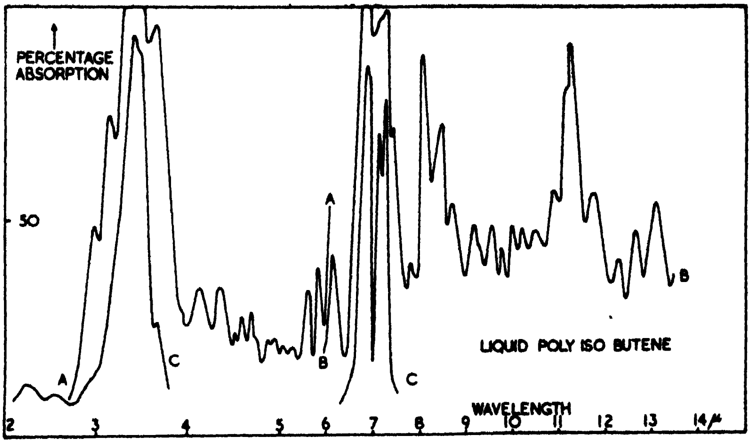
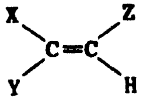


Figure 1

from the main polymer chain. Thus the bands due to the end groups may be easily identified as those not occurring in the generally accepted spectrum of polyisobutene (7). Two prominent bands of this type occur at 6.09 and 11.1 μ. The former is due to a C=C valency vibration and the latter to an out-of-plane vibration of the hydrogen atoms in a $^{X}_{Y}\!>C{=}CH_2$ group (7,8). The absence of these bands from the spectrum of the polyisobutene of high molecular weight, and their presence in our polymer proves that the chain-termination reaction 3a is occurring. On the other hand, unsaturation of the type:



postulated in equation 3b might be expected to give rise to a band at about 12 μ (7). There is a weak band at 12.24 μ, which could be due to such groupings, but its weak intensity means that such end groups, if present at all, are very infrequent compared with those formed in reaction 3a. Further evidence against the presence of the equation 3b end group is that no sign of any absorption has been detected at 5.97 μ corresponding to the stretching vibration of a C=C link of this type (9).

The second outstanding difference between the spectra of the high- and low-molecular polyisobutene polymers is the presence in the latter of a pair of bands at 8.00 and 8.38 μ, which are known to be characteristic of a $-C(CH_3)_3$ group at the end of a hydrocarbon chain (10). This band is absent from the spectrum of the high polymer, which instead exhibits a single band at 8.2 μ. Thus the mechanism of initiation (equation 1a) is confirmed. The absence of bands at 8.8 and 8.55 μ, which are to be associated with terminal isopropyl groups (10), suggests that reaction 1b is not responsible for the initiation of many of the reaction chains.

The foregoing conclusions concerning the presence of the:

$$-C(CH_3)_3 \quad \text{and} \quad C{=}CH_2$$

end groups are based on intense bands and well-established correlations backed by theoretical calculations. Certain other conclusions can be drawn which for the time being should be regarded as carrying less weight since they are based either on weak bands or less well-established correlations. For example, since reaction la occurs, the end grouping $(CH_3)_2\dot{C}\ CH_2D$ is to be expected when D_2O is used as cocatalyst, and the C-D band in this group might give a weak band near 4.6μ. Two weak bands are found in (A) at 4.58 and 4.68μ. Either or both of these may be C-D stretching frequencies. If the latter turns out to be the case, then the alternative mechanism lb may be occurring occasionally. This point requires further investigation. The presence of weak bands at 2.98 and 3.13μ indicates that OH groups are present in which the H atoms are hydrogen bonded. These are to be expected as the D_2O of the complex is converted to HOD and H_2O in successive cycles of reaction. There are also very weak bands at 4.14 and 4.34μ, which may well be due to OD groups with the D atoms "deuterium bonded." These may be due to a small fraction of cocatalyst molecules originally present, which have not been required to initiate chains, and have not therefore undergone any isotopic exchange. That such a fraction of unchanged cocatalyst molecules exists, although the number of polymer molecules formed for each molecule of cocatalyst present is very large (about 50), is entirely consistent with the catalyst regeneration implicit in the occurrence of reaction 3a. If reaction 4 takes place some cocatalyst will be destroyed, but also C-OD and C-OH groups should occasionally be present. Since such groups present in other tertiary alcohols give an intense band at 8.7μ and a weak band is found in this neighborhood we cannot, at this stage, completely exclude the possibility of reaction 4 occurring to a very limited extent. Further investigation using longer path lengths would enable us to be more precise on this point.

Both the firm and the tentative conclusions mentioned in the preceding paragraphs substantiate the mechanism for this reaction put forward by Polanyi and co-workers (3) and exclude those (2) which do not ascribe the catalytic action to the acidic (i.e., proton donating) power of the catalyst-cocatalyst complex.

The above results and conclusions have been put on record to indicate the potentialities of the infrared method in the elucidation of problems of the mechanism of polymerization. Another example is the detection* of terminal hydroxyl groups in the products of polymerization of nitriles in aqueous solution initiated by hydroxyl radicals made either by photodissociation of hydrogen peroxide, or by the action of x- or alpha-rays on water (11). The results on this are still incomplete, and will be published later together with further investigations along these lines.

Acknowledgment

We gratefully acknowledge the loan of the spectrometer on which these results were obtained from Messrs. Aero Research Ltd. and we are indebted to the Royal Society for financial assistance.

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*Experiments carried out with Dr. D. A. Ramsay.

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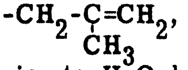
Synopsis

Measurement of the infrared absorption spectrum of the low-molecular liquid polymer formed at room temperature from gaseous isobutene using BF_3 as a catalyst and D_2O as a cocatalyst indicates that the dominant end groups in the final polymer are $(CH_3)_3C$ and  $-CH_2-\underset{CH_3}{C}=CH_2$, and that the cocatalyst D_2O undergoes partial conversion to H_2O during reaction. These results substantiate the mechanism advanced by Polanyi and others, namely: (a) initiation through formation of the trimethyl carbonium ion by acceptance by isobutene of a proton (or deuteron) from the catalyst-cocatalyst complex, and (b) termination by expulsion of a proton from a methyl group to the anionic complex fragment, with corresponding catalyst regeneration, i.e.:

$$\sim\!\sim CH_2-C^+(CH_3)_2 + BF_3.OD^- \longrightarrow \sim\!\sim CH_2-C(CH_3):CH_2 + BF_3.HOD$$

Résumé

Les auteurs ont mesuré le spectre d'absorption infra-rouge du polymère liquide, de poids moléculaire peu élevé, obtenu à température de chambre au départ d'isobutène, en présence de BF_3 comme catalyseur, et D_2O comme cocatalyseur. Ces mesures indiquent que les groupes terminaux dominant dans le polymere final repondent aux formules $(CH_3)_3C$ et $-CH_2-\underset{CH_3}{C}=CH_2$; d'autre part, elles indiquent que

le cocatalyseur D_2O se transforme partiellement en H_2O au cours de la réaction. Ces résultats appuient le mécanisme proposé par Polanyi et autres, savior (a) une initiation de la réaction par formation d'ion triméthylcarbonium, par addition à l'isobutène d'un proton (ou deuteron), provenant du complexe catalyseur-cocatalyseur, et (b) la terminaison de chaîne par expulsion d'un proton d'un groupe méthyle vers un fragment anionique complexe, avec régénération du catalyseur correspondant, c.a.d.:

$$\sim CH_2-C^+(CH_3)_2 + BF_3.OD^- \longrightarrow \sim CH_2-C(CH_3):CH_2 + BF_3.HOD$$

Zusammenfassung

Messungen der infraroten Absorptionsspektra der niedrig molekularen fluessigen Polymeren, die bei Raumtemperatur aus gasfoermigen Isobutylen unter Benutzung von BF_3 als Katalysator und D_2O als Kokatalysatot gebildet wurden, zeigt, dass die dominierenden Endgruppen im Endpolymer $(CH_3)_3C$ und $-CH_2-\underset{CH_3}{\underset{|}{C}}=CH_2$ sind und dass der Kokatalysator, D_2O einer teilweisen Umlagerung zu Wasser waehrend der Reaktion unterliegt. Diese Resultate bestaetigen den Reaktions verlauf, der von Polanyi und anderen vorgeschlagen wurde, naemlich (a) Startreaktion durch Bildung des Trimethyl-Carboniumions durch Aufnahme eines Protons oder Deuterons an Isobutylen von dem Katalysator-Kokatalysator-Komplex, und (b) Endreaktion durch Ausstossung eines Protons von der Methylgruppe zum anionischen Komplexbruchstueck, unter Regenierung des Katalysators, zum Beispiel:

$$\sim CH_2-C^+(CH_3)_2 + BF_3.OD^- \longrightarrow \sim CH_2-C(CH_3):CH_2 + BF_3.HOD$$

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Photochemistry of Proteins. V. Effect of pH and Urea on Ultraviolet Light Inactivation of Crystalline Pepsin*

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INTRODUCTION

Pepsin is readily inactivated by heat or by ultraviolet light (1). That the rate of destruction by light follows the "monomolecular" course was shown by Hussey and Thompson (2), Northrop (3), and Gates (1). Pincussen and Uehara (4), Hussey and Thompson (2), Collier and Wasteneys (5), and Northrop (3) noted a pronounced effect of hydrogen ion activity on the rate of pepsin inactivation by ultraviolet radiation. They placed the pH of optimum rate at 1.4, 1.15, 1.9, and about 2.0, respectively. The inactivation of pepsin by light has also been reported by Calvin (6) Giri (7), and Burge, Fischer, and Neill (8). An historical account of these studies may be found elsewhere (9).

It has been claimed that the number of tyrosine groups in pepsin accessible to iodination increases with the addition of urea although the activity was not thought to decline with this increased accessibility (10). Modification of tyrosyl residues results in loss of activity (11). If the former is true, the increased accessibility of tyrosine any screening effect of chromophoric groups about the vital tyrosine residues and the quantum yield would expectedly be higher in the presence of urea (12). This has been investigated.

For the inactivation of pepsin, Gates believed that there is a direct correspondence between the inactivation spectrum and the absorption spectrum. He gives a misleading value of unity for the quantum yield whereas, by calculation from Gates' data, Landen has shown that lower values are obtained which are not constant with wave length (13). Interpolating from the calculations of Landen, one sees that 0.00036 is more consistent with the data of Gates at 2537 A. than is unity (14). Unfortunately the data of Gates is not self-consistent and it seemed, therefore, worthwhile to establish the quantum yield for pepsin at 2537 A. as a function of pH with hemoglobin (used by Gates). at pH 2.01, casein was also used as a substrate.

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*From the Master of Science Thesis of S. Pearson, Polytechnic Institute of Brooklyn, June, 1948.

EXPERIMENTAL

Pepsin. Crystalline pepsin, containing magnesium sulfate,* was obtained from the Plant Research Laboratories, Lehn & Fink Products Corporation. These producers state that the crystalline enzyme was prepared from pepsin (U.S.P. XI) (from the stomachs of swine) and was free of any other enzymes. The sample was free of nitrogen-containing impurities and was 47.9% pepsin calculated on the basis of 15.4% nitrogen (15) in pure pepsin.**

Pepsin stock solutions were prepared from 0.1 M sodium acetate solvent containing either acetic acid or hydrochloric acid to obtain the desired pH. A Beckman glass electrode pH meter was used throughout for measuring hydrogen ion activities of the pepsin solutions. Enzyme solutions of pH values less than 5 were stable for several days if kept at 5°C. Solutions of pH 5.5 and higher were used within three hours after preparation, since such solutions undergo inactivation on standing (16–19).

Hemoglobin Substrate and Activity Curves

The hemoglobin substrate (20) was prepared by whipping fresh beef blood until no additional clot formed. The mixture was filtered through gauze and the filtrate was centrifuged. The supernatant liquid was removed by suction and to the residue was added an equal volume of 1% aqueous sodium chloride. After inverting the mixture several times and centrifuging, the supernatant liquid was again removed. The hemoglobin was dialyzed in a 3/4-inch diameter du Pont cellophane tubing for 24 hours, frozen, and stored in the frozen state. A substrate solution was prepared for each experiment by diluting 40 parts of a 2.5% hemoglobin solution with 10 parts of 0.3 N hydrochloric acid. The substrate solution was always used within one hour of preparation.

For the activity curves of crystalline pepsin, a series of dilutions was prepared of the stock solutions using 0.01 N HCl. 1 ml. of each diluted solution was then added to 5 ml. hemoglobin substrate and digested at 24.1°C. After 10 minutes the enzyme was undigested protein were precipitated by adding 10 ml. 0.3 N trichloroacetic acid and centrifuging. The products of the digestion in the supernatant liquid were then reacted with the phenol reagent of Folin and Ciocalteau (21) and determined according to the method of Anson (20) with one change. The use of a Klett-Summerson photoelectric colorimeter, in conjunction with a No. 66 filter transmitting 6400 – 7000 A. light, in the colorimetric determination of split products obviated the need for the addition of tyrosine to the blanks as recommended by Anson. An example of this procedure is given in Table I. The calculated concentrations were obtained by dividing the colorimeter reading of the diluted solutions by that of the most concentrated solution, and multiplying this fraction by the concentration of the standard solution. The discrepancy is of the order of 5%.

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*The term "crystalline pepsin" means pepsin plus magnesium sulfate in this paper.

**Nitrogen was determined by the micro-Kjeldahl method, courtesy of Mr. A. Heisler.

TABLE I. Variation Of Pepsin Activity On Hemoglobin With Enzyme Concentration

Concentration of crystalline pepsin, mg./ml.	Colorimeter reading	Calculated concentration
1.33	235	-
1.00	178	1.01
0.80	147	0.82
0.67	112	0.64
0.33	57.2	0.32
0.13	24.1	0.14

Casein Activity Curve

The method used was essentially that used by Kunitz (22) to measure trypsin activity, with a minor modification. Pepsin is inactive in alkaline media, so casein was dissolved in approximately M/15 phosphoric acid. Pepsin solutions were allowed to digest the casein at 37°C. for 30 min. at pH 2.01. Dilutions of standard crystalline pepsin solutions were prepared as described above. 1 ml. of each dilution was used to digest 1 ml. of the casein substrate of a constant but arbitrary concentration. After digestion and precipitation with trichloroacetic acid, the mixture was kept at room temperature for at least two hours, centrifuged, and decanted. The density of the supernatant liquid was measured at 2800 A. with a Beckman spectrophotometer.

Irradiation Methods

An Hanovia Sc-2537 mercury resonance lamp* was employed. The lamp was made from a fused quartz tube 28 cm. long between electrodes and bent at two right angles 10 cm. from the electrodes. The U-shaped arc was mounted in a horizontal position, the radiation from the short, straight portion being used. In order to be able to vary the solution to arc distance, the arc was mounted on a movable frame; the frame in turn was attached to a sliding rail which could be moved toward or away from the solutions. A luminous sign transformer** having a secondary coil rated at 5000 volts and 60 milliamperes activated the lamp.

At a distance of 3.5 cm. from the lamp a fused quartz cell*** of 1-cm. depth and 26-mm. inside diameter was mounted in a 4.2-cm. block, drilled to fit, and also mounted on a sliding rail. The quartz cell was equipped with two arms, each 6-mm. inside diameter, at an angle of 45° with each other. Through one arm passed a fused quartz stirrer, driven at 150 r.p.m. by a toy motor, **** and prepared by twisting the flattened end of a 3-mm. diameter fused quartz rod. From the other arm, samples of irradiated enzyme could be withdrawn peridically. The lamp-to-block distance is critical because at 3.5 cm. the inverse square law of intensities does not hold with a lamp of this size which is not a point source. Between the lamp and the two-armed cell was placed, in a similar block, another quartz cell which contained 43% acetic acid. It has been shown that this filter of 1-cm. depth transmits only 11.5% of the 2483 A. line, and virtually nothing shorter than 2450 A. (23). A 2% acetic acid filter transmits 98% at 2537 A. and 94% at 2483 A. A trace of energy has been shown to occur with the Sc-2537 lamp at 2483 A. (13) although none is reported by the manufacturer. The fact that the same quantum yield was obtained with either filter, as a test, is proof that the amount of energy at 2483 A. is neglibible, since the ratio of energies at 2483 and 2537 A. is different with the two filters. The spectral energy distribution of the lamp in microwatts per square centimeter at 20 inches as given by the manufacturer for an input of 25 watts is summarized in Table II.

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*Hanovia Chemical Manufacturing Co., Newark, N. J.

**Jefferson Electric Company, Bellwood, Illinois.

***American Instrument Company, Silver Springs, Md.

****An Erector set motor, A. C. Gilbert Co., New York, is admirable for the purpose.

TABLE II. Spectral Energy Distribution Of Sc-2537 Lamp

Wave length, A.	Microwatts	Wave length, A.	Microwatts
4000-7000	4.0	2800	Trace
3660	0.3	2650	Trace
3130	0.2	2537	40.0
3025	Trace	2260	0.2
2967	Trace		

At wave lengths greater than 2860 A. no inactivation was found to occur (1) and therefore no filter was needed for the Sc-2537 lamp for radiation longer than the 2537 A. reasonance line.

Intensity measurements were performed by both physical and chemical methods. For the physical method a C-423 lamp from the National Bureau of Standards was used as primary standard along with an Eppley, bismuth-silver, linear, vacuum thermopile with a quartz window* and a Leeds and Northrop No. 2284 high-sensitivity galvanometer,** with a circular scale at 1 meter. For this setup a 1-cm. deflection represented 9.84 X 10^{-6} watts/cm.^{2}. With the reaction cell empty and with the arc at 10 cm. a deflection of 29.6 cm. was obtained with the thermopile mounted directly behind the cell. With the cell full of a 0.014 M solution of phenylacetylalanine, which absorbed over 99% of 2537 A., a deflection of 5.5 cm. was observed. This checks with the manufacturer's statement that approximately 85% of the generated light is at 2537 A. By correcting for reflections, using the formula of Bowen (24), the intensity absorbed by the solution was found to be 87.6 X 10^5 ergs/cm.^{2}/hour. This corresponds to 1.86 X 10^{-6} einstein/cm.^{2}/hour at 2537 A. No correction was made for lack of parallelism of the beam.

Using the uranyl oxalate actinometer method and a formula of Bowen (24) the value of 1.74 X 10^{-6} Nhν per cubic centimeter per hour was found. In the procedure of Bowen, a dilute uranyl oxalate solution is used at 2537 A. which, however, absorbs all the light at that wave length. At 3500 A. only 10% and at 4046 A. only 5% of the incident intensity is absorbed. Taking these percentages into account along with the data of Table II, one can easily calculate that with this actinometer the error in intensity at 2537 A. is not off by more than 2% of the true value.

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*The Eppley Laboratory, Inc., Newport, R. I.

**Leeds and Northrop Company, Philadelphia, Pa.

The agreement of the two methods is considered satisfactory in view of the errors of genometric origin in the physical measurements. Inasmuch as most of the experiments were performed with the arc at 3.5 cm. from the reaction cell and the actinometer measures the number of Nhν falling on the solution in the cell during the exposure time (no corrections are required for the fact that the incident light is not parallel, etc., as is required for the physical method), the intensities used in the calculations of quantum yields are those based on actinometer measurements. It is significant that at 10 cm. the same quantum yield for chymotrypsin was found as at 3.5 cm. with this setup (25).

For the exposures, 4 ml. of solutions of crystalline pepsin in 0.1 M sodium acetate adjusted to the requisite pH with hydrochloric acid were utilized. At intervals, small samples were withdrawn for activity measurements. The percentage losses in activity were found by comparison with the activity of an unirradiated portion of crystalline pepsin solution: the colorimeter reading obtained by use of the irradiated solution was divided by the colorimeter reading obtained by the use of the unirradiated solution and the ratio was multiplied by 100. Since the pepsin activity curve obtained with hemoglobin is a straight line in the range of pepsin concentrations used (e.g., Table I), this value equals the per cent activity remaining after irradiation. A separate, unirradiated solution was used with each series of exposures. With the equipment used the solutions were always irradiated at room temperature; no heating of the solutions occurred during the exposures.

A few exposures of enzyme solutions, in quartz test tubes with soft glass test tubes holding solutions as controls, to an Hanovia Sc-1558 Utility Lamp were made in order to study inactivation rates as a function of pH with polychromatic light.

Absorption Measurements

The percentage absorptions of the enzyme solutions were measured with a Beckman quartz spectrophotometer, using cells of 1-cm. depth, against the acetate buffer. Absorption by the buffer at 2537 A. was between 1 and 2% and considered negligible. The absorption of 4 M urea in buffer was 17%.

Effect of Urea on Pepsin Activity

Pepsin in urea - 0.1 M sodium acetate was allowed to stand at room temperature. At intervals, aliquots of solution were removed and the activities were measured toward hemoglobin. At the same time the activity of a pepsin solution of the same pH and pepsin concentration, which had been standing for an equal length of time at the same temperature, was measured. At pH 5.72, it was found that 4 M urea seemed to reduce the activity of pepsin. This effect could be a result of any one, or combination, of three things. The urea could modify the reaction between tyrosyl containing split products and the phenol reagent causing a decrease in the intensity of color produced per unit of tyrosine. It was found that urea did not modify this color reaction. The urea could modify the hemoglobin and thereby reduce the rate of digestion by pepsin, or the urea could inactive pepsin. The latter was found to be the case; the activity of pepsin decreased on standing in urea solutions. That the properties of hemoglobin as a substrate are not affected by urea has been noted by Steinhardt (26).

RESULTS

Absorption Spectra

The ultraviolet absorption spectrum of our pepsin sample is almost the same as that of Gates (27). The molecular extinction coefficient is defined as:

$$\varepsilon = 1/Cl \ (\log_{10} I_0/I) \tag{1}$$

where the concentration C is in moles per liter and l is the path length (of 1 cm.). Gates found $\varepsilon_{\text{min.}}$ to be between 20,000 and 25,000 at 2500 A. and an $\varepsilon_{\text{max.}}$ in the neighborhood of 60,000, at pH 5.0. Our values are $\varepsilon_{\text{min.}} = 18{,}500$ at 2500 A. and $\varepsilon_{\text{max.}} \cong 52{,}000$ at 2700 A. at pH 5.08 (initial value, before irradiation). Gates states that irradiation did not greatly affect the peak at 2775 A. and that the valley at 2500 A. filled up. Our data (Table III) shows that the valley does tend to fill up but that the peak at 2700 A. also increases. For an equal degree of inactivation, these changes with irradiation are more pronounced at pH 5.08 than at pH 2.62.

Gates also reported that heat denaturation of pepsin did not result in a significant change in the absorption spectrum after a loss of 56.5% activity. We have found that 7 M urea (pH 5.48) will inactivate pepsin at room temperature and that the changes in absorption of light by the pepsin solutions are less marked than with light inactivation (Table III). It was found, however, that appreciable inactivation occurred in the presence of 7 M urea without any change in absorption. The change in absorption may, therefore, result form secondary reactions. That the mechanisms of heat, light, and urea inactivations are different is indicated.

Quantum Yield as Function of pH

The quantum yield (ϕ) is given as:

$$\phi = cf/MI_0F \tag{2}$$

where c = concentration in grams pepsin per milliliter, f = fraction of molecules inactivated during the time of irradiation, M = molecular weight of pepsin (28) = 35,500, I_0 = Nhν falling on the solution per cubic centimeter during the time of irradiation, and F = fraction of light absorbed by protein at 2537 A. corrected for the average amount absorbed by active protein during the irradiation. The correction factor is given by $\bar{E}/E_0$ where E_0 is the initial concentration of enzyme in moles per cubic centimeter and $\bar{E}$ is the average amount of active enzyme during the exposure. The latter amount is given by:

$$\bar{E} = E_0/t \int_0^t e^{-kI_0 t} \, dt \tag{3}$$

TABLE III. Changes in Transmission of Pepsin Solutions Accompanying Inactivation by Ultraviolet Light and by Urea.[a]

	Loss in activity by **ultraviolet** light				Loss in activity by 7 M urea		
	Inactivation, %				Inactivation, %		
Wave length, A.	0	42	0	46	15	23	40
	Percent transmission **at** pH 2.62		Percent transmission at pH 5.08		Percent transmission at pH 5.48		
3100	93.3	76.1	93.8	67.1	95.8	94.8	86.9
3000	79.8	61.8	77.1	49.6	78.9	78.1	72.9
2900	34.2	27.1	31.2	19.9	32.7	32.2	29.9
2800	15.1	12.1	13.2	8.1	14.2	14.1	12.8
2700	19.2	14.8	17.8	10.5	18.7	18.3	16.1
2600	34.8	25.6	33.2	19.2	35.2	34.2	29.8
2537	45.9	33.3	44.3	25.9	47.1	46.1	39.3
2500	48.9	35.2	47.1	26.8	50.9	49.3	42.2
2475	46.8	33.7	44.8	24.5	48.0	46.2	40.1
2450	40.8	29.1	38.2	20.8	41.2	40.7	35.0
2400	16.2	11.7	14.0	7.1	15.1	15.0	13.8

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[a] Concentration of pepsin, 0.623 mg./ml.

TABLE IV. Variation of Quantum Yield (ϕ) with pH at 2537 A.

pH	Concentration,[a] mg./ml.	Absorption at 2537 A., %	I_0 as $Nh\nu \times 10^4$ per ml.per hr.	Time of irradiation, min.	Inactivation, %	$\phi \times 10^3$
2.01	0.60	31.8	0.156	10	20.9	2.30
				20	37.2	2.30
				30	49.7	2.24
	1.33	57.1		10	18.7	2.53
				20	34.4	2.56
				30	47.2	2.49
						Av. 2.4
2.66	1.45	60.3	0.162	10	24.3	3.34
				20	46.4	3.74
				30	56.3	3.31
	1.30	56.1		17	42.4	Av. 3.5
3.18	1.31	56.6	0.197	10	27.2	3.03
				20	40.2	2.43
				30	53.0	2.38
			0.180	15	32.9	2.75
				15	30.6	2.53
				25	42.5	2.29
				25	47.9	2.70
	1.22	54.0		10	26.6	3.12
				20	42.6	2.80
						Av. 2.7

4.08	1.31	56.6	0.197	10	18.3	1.88
				20	32.8	2.11
				30	48.7	1.92
			0.180	20	26.7	1.61
						Av. 1.9
5.04	1.31	56.6	0.197	10	20.2	2.04
				20	35.0	1.95
				30	46.1	2.14
	1.30	56.1	0.162	30	46.2	2.38
						Av. 2.1
5.96	1.22	54.0	0.180	15	33.7	2.83
				25	51.0	2.97
				10	25.2	2.93
				20	38.9	2.49
	1.31	56.6	0.175	10	23.8	2.92
				20	40.4	2.76
				30	56.2	2.94
						Av. 2.8
6.02	1.31	56.6	0.180	20	67.3	5.78
				30	80.2	5.48
				15	59.8	6.29
				25	78.3	6.33
						Av. 6.0
6.18	1.31	56.6	0.175	10	48.9	7.17
				20	74.5	7.27
				30	87.8	7.46
						Av. 7.3

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[a] Concentration of crystalline pepsin (pepsin plus magnesium sulfate).

The correction factor may be used provided (a) that a "one-hit" inactivation occurs (29) and (b) that the products and reactants have the same molecular extinction coefficients.

From equations 1, 2, and 3 it can be shown that the quantum yield is also given by:

$$\phi = \frac{E_0 \ln \frac{100}{\%A}}{(Nh\nu)\text{ absorbed}} \qquad (4)$$

where A is the per cent activity remaining at time t. With pepsin, for a 10% loss in activity, the absorption at 2537 A. for the solutions used increased by about 5%. Nevertheless, ϕ values as calculated by equation 2 or 4 gave nearly constant values for even higher degrees of inactivation, (Table IV). Throughout the work, first-order kinetics of inactivation were encounted durin irradiation. Obviously the use of equation 4 is more convenient, since the use of equation 2 requires either a solution of equation 3 or a graphic estimate.

The results of the calculations at the hydrogen ion activities studied, with hemoglobin as a substrate, are summarized in Table IV. No change of pH of pepsin solutions was found to occur during irradiations.

Quantum Yield Dependence on Nature of Substrates

The quantum yield at pH 2.01 was determined based on a loss of activity toward both hemoglobin and casein. The results are tabulated in Table V. The same quantum yield was found with either substrate.

TABLE V. Effect of Ultraviolet Light (2537 A.) on Pepsin Activity toward Hemoglobin and Casein.

Irradiation time, min.	Inactivation, %	Quantum yield $\times 10^3$
With Hemoglobin as Substrate		
10	18.7	2.53
20	34.4	2.56
30	47.2	2.49
		Av. 2.53
With Casein as Substrate		
10	21.8	2.84
20	36.1	2.57
30	45.2	2.31
		Av. 2.57

Effect of Urea on Quantum Yield

Li postulated that the steric arrangement of tyrosine groups in pepsin is not essential for proteolytic activity, though modifications of these groups destroy activity (10). This came about as a result of iodination experiments in which Li found some "unavailable" tyrosine groups to become available in 7.1 M urea, pH 5.7, without, supposedly, the urea causing denaturation of pepsin. This concentration of urea was not considered to bring about denaturation because 4 M urea, near pH 2, did not cause inactivation of pepsin (26).

Should these findings be true, the quantum yield for inactivtion might expectedly be higher in the presence of urea.

It has now been found that the activity of pepsin solutions decreases on standing in 4 M to 7 M urea solutions, at pH 5.0 and higher (Table VI). This inactivation is a complicating factor apparently not considered in Li's experiments concerning the iodination of pepsin in urea solutions.

TABLE VI. Effect of Standing in Urea Solution on Pepsin Activity

Concentration crystalline pepsin, mg./ml.	pH	Urea concentration	Time, min.	Inactivation, %
0.5	5.00	4 M	60	6.7
			150	12.2
		7 M	60	24.0
			150	32.7
1.30	5.48	7 M	5	13.3
			30	19.8
			60	23.2
			1418	40.7
1.33	6.02	5 M	8	27.8
			230	43.7
			1340	74.8

The effect of urea on the quantum yield of pepsin at pH 3.18, 3.29, and 5.72 was measured. 4 M urea did not modify the activity, absorption of light, or rate of inactivation of pepsin by ultraviolet light at pH 3.18 or 3.29. At pH 5.72, it was found that 4 M urea did not influence absorption or, apparently, the quantum yield, but it did reduce the activity of pepsin (Table VII).

DISCUSSION

The quantum yield at pH 2.01, namely 0.0024, is considerably higher than the values calculated by Landen from the data of Gates. This may in part be due to the fact that our solutions were stirred during the exposures. Our recalculations of the data of Gates is summarized in Table VIII.

The quantum yield consistently decreases at each wave length with increasing irradiation; this, coupled with the knowledge that the extinction coefficient increases during inactivation, allows one to conclude that lack of stirring may have been partially responsible for the lower values of ϕ to be gleaned from Gates' data. His data gives a value at 2509 A. about one-third of our value at 2537 A. Incidentally, the fact that the quantum yields vary with wave length (Table VIII) is doubtless the reason for the poor fit of Gates' action spectrum with his absorption spectrum (1).

The question naturally arises as to the meaning of a quantum yield of 0.0024. On the average only one quantum out of $\sim$ 400 is ef-

TABLE VII. Results of Exposure of Pepsin in Urea Solution to Ultraviolet Light.

Crystalline pepsin concentration, mg./ml.	pH	Urea concentration	Time of irradiation, min.	Colorimeter reading	Inactivation, %
1.22	3.18	0 M	0	181	-
			10	133	26.6
			20	104	42.6
		4 M	0	177	-
			10	132	25.4
			20	98	44.7
1.02	5.72	0 M	0	210	-
			10	168	20.0
			20	152	26.7
		4 M	0	129	-
			10	100	22.4
			20	87	32.6

TABLE IX. Quantum Yields for the Photolysis of the Peptide Bond (2537 A.).

Compound	ϕ based on alanine liberated	ϕ based on ammonia liberated	ϕ
Acetyl-DL-alanine	-	71.5×10^{-3}	71.5×10^{-3}
Phenylacetyl-DL-alanine	4.77×10^{-3}	2.27×10^{-3}	7.04×10^{-3}
Phenylpropionyl-DL-alanine	0.89×10^{-3}	5.91×10^{-3}	6.80×10^{-3}

fective. Since these quanta are absorbed by the aromatic residues, phenylalanine, tryptophane, and tyrosine, of which there are 33 aromatic residues per molecule (30), one wonders as to whether some particular aromatic residue must absorb a quantum to produce inactivation of the molecule, with a yield of around 0.08, or whether any aromatic group may do so, but with a yield of about 0.0025. Recently, Levy has acquired data for the photolysis of phenylacylalanines (23). Some of her results are summarized in Table IX. It is seen that for the grouping most similar to that in a protein, namely phenylpropionylalanine, the yield is around 0.007, and, unless the quantum efficiency for a similar linkage is ten times higher in a protein, we may suppose that the former possibility is improbable.

TABLE VIII. Quantum Yields Calculated from the Data of Gates

Point-wave length, A.	Inactivation, %	Quantum yield
2357	31.4	2.92×10^{-3}
	50.0	2.55
	54.4	2.52
2509	17.3	8.60×10^{-4}
	41.0	6.72
	50.0	6.09
2719	15.6	10.1×10^{-4}
	26.0	8.41
	50.0	7.46

Inactivation could also involve cleavage of -S-S- bonds, a host of hydrogen bonds, or alteration of benzenoid groups. More data must be acquired before a detailed mechanism of inactivation can be offered.

With trypsin, Verbrugge has speculated as to the existence of more than one active center per molecule. He found that he did not obtain the same quantum yield using the hemoglobin method as he did with casein as a substrate. With pepsin we have found no difference in quantum yield. Verbrugge also speculates that pepsin has more than one active center (31). Since Northrop (3) established the fact that loss of activity of pepsin during irradiation was proportional to loss of solution protein (pepsin digested the inactivated, denatured form), it can be seen that inactivation by light is an "all or none phenomenon." The use of ultraviolet light, with pepsin at least could not be expected to give rise to any preferential breakdown of active centers if there be, indeed, more than one, either alike or dissimilar, active center per molecule.

Rate of Inactivation

Collier and Wasteneys (5) found that the "velocity of destruction" of pepsin varied with pH; the rate showed a maximum near pH 2, a minimum near pH 4.75, and a rapid rise toward infinity at approximately pH 6.8. This could be attributed to changes in the molecular extinction coefficient, to variation of quantum yield with pH, or to changes of the relative efficiencies of the components of polychromatic light (used by Collier and Wasteneys) with pH. Our findings show a nearly constant value of the molecular extinction coefficient in the pH range studied. The inactivation of pepsin by ultraviolet light is a monomolecular reaction. For any incident intensity, I_0, we may write:

$$K = 1/t \ln(100\%/\%A) \tag{5}$$

The observed rate constants at the pH's studied are not comparable because the intensities employed varied from experiment to experiment. Comparable rate constants may be calculated from quantum yields at each pH by assuming arbitrary values for E_0 and I_0 and by substituting these values and a corresponding calculated value of percent absorption into the equation:

$$K = 1/t \ln(100\%/\%A) = \phi I_0(\% \text{ absorption})10^{-2}/E_0 \tag{6}$$

For example, taking the concentration of pepsin protein as 1.75×10^{-8} moles per cubic centimeter, the intensity as 10^{-5} Nhν per hour per cubic centimeter falling on the solution, the absorption as 56.1%, $\phi = 2.4 \times 10^{-3}$, and t in hours, one obtains K = 0.81 at pH 2.01. The variation of K with pH is shown in Figure 1. It is observed that at 2537 A. maximum rate of inactivation is observed to be at pH between 2 and 3, rather than at pH 2 as found by Collier and Wasteneys (5). Further these authors found K at pH 2 to be 1.7 times the value at 3, whereas our values at these pH's are about the same. It seemed possible that these divergent findings might be attributable to a greater variation of ϕ as a function of pH at wave lengths other than 2537 A. Collier

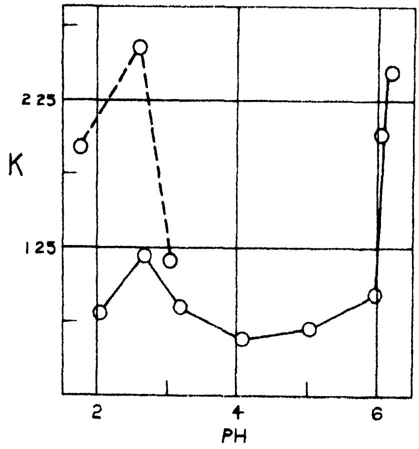

Fig. 1. Rate of inactivation, K, as a function of pH with monochromatic light (solid line) and with polychromatic light (broken line).

and Wasteneys used a full mercury arc with which destruction was attributed to the region 2000-3130 A. For a test, pepsin solutions were exposed to the full light of a mercury arc in quartz test tubes. The rates at three pH values are also plotted in Figure 1. Since this polychromatic source has appreciable intensities at 3130, 3025, 2803, 2699, 2654, 2482, and 2399 A., as well as at 2537 A. (according to the manufacturer), it may be concluded that the quantum yield is a more marked function of pH at some other wave lengths than 2537 A. It may be pointed out that K at pH 1.6 is greater than at pH 3.05 in qualitative agreement with Northrop's finding (3), and that Collier and Wasteneys did not use pure pepsin and found variations among samples. It is well known that foreign proteins "protect" enzymes from irradiation.

Pepsin is a relatively strong acid having apparently no isoelectric point. This extreme acidity for a protein is apparently only partially attributable to a phosphate residue (30). Its pH range of maximum thermal stability is 4.5 to 5.5 (32,33). Steinhardt and others have shown that pepsin inactivation, on standing in solution at pH's on the alkaline side of its pH stability maximum, increases rapidly with increasing pH toward 7. This inactivation is partially reversible by adjustment to a more acid pH. It has been reported that most of the acidic groups of pepsin are not ionized below pH 4.5 (34). Above pH 4.3, Conn et al. (35) and Herriott et al. (30,36) found a smooth change in pH with addition of potassium hydroxide to over pH 9. Herriot et al. found a definite ionization above about pH 2.7, however. Between pH 6.2 and 6.8, pepsin activity, upon the addition of alkali, drops from 100 to 70%; the "heat of denaturation" falls from 79 to nearly 0% of its value at pH 4.3 (35). Steinhardt found a 100- fold increase in rate of inactivation from pH 5.8 to 6.2 (19). The activity of pepsin is apparently associated with the un-ionized form (neglecting the phosphate residue) for the pH region for optimum activity toward proteins which is generally 1.5 to 2*. It is pH 4.0 for the cleavage of carbobenzoxyglutamyl- tyrosine, however (37). The rate of inactivation of pepsin by light shows relatively low values between pH 3.6 and 5.3, with a minimum near pH 4.2 or 4.3. This is in the region of maximum thermal stability (38) at which point pepsin probably has a maximum number of salt bridges. With the addition of alkali the number of un-ionized carboxyls (from glutamic acid residues) decreases and a strong repulsion between ionized groups becomes operative. (The number of basic groups (30) is small in pepsin, 4–6, as compared with the number of carboxylic acid groups, $\sim$ 28.) This is analogous to the titration of polymethacrylic acid to which a similar statement applies (39). In this strained, ionized condition, less activation energy is required for breakdown than is required if the molecule must first acquire energy for the ionization of the five ionizable, probably cystenylamino, groups postulated by Steinhardt (19).

We may visualize the photochemical step as consisting of cleavages of -S-S- or a -CONH- bond. There will be a decrease in the tendency for the resulting radicals to recombine because of the ionic repulsion of the large, charged fragments at a pH above 5; a higher quantum efficiency is therefore observed. If this is true, one might expect a lower quantum yield by irradiation under pressure of four to five thousand p.s.i.* The increasing failure of radical split products to recombine with increasing pH means a decrease in a Franck-Rabinowitch effect. The increase of quantum yield with increasing frequency (Table IX) also points in the direction of a decreasing Franck-Rabinowitch effect (40).

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*Pincussen (4) suggested the determination of the pH for optimum destruction by ultraviolet radiation as a method of measuring the pH for optimum activity of enzymes. This is probably not general and has not been found true with chymotrypsin (25).

It is quite possible that with protein molecules which are held together at many points there may be an internal Franck-Rabinowitch effect operating, i.e., two free-radical fragments may be held in place by the protein framework until recombination can take place or until reaction with the solvent, etc., takes place.

At present we can offer no explanation for the rise in the quantum yield to what appears to be a maximum near pH 2.65. Below pH 2, pepsin may be an equilibrium mixture of native and denatured protein, as in postualted for trypsin above pH 9 (30), and the action of light on the denatured form may proceed more slowly than with the active protein. Photochemical experiments with peptides as a function of pH may be helpful. It is interesting to note that the rates of deamination of alanine and aspartic acid show a minimum near pH 6 and rise toward pH 2 with exposure to light from a mercury arc. The effective wave lengths, in the absence of a photosensitizer, may be less than 2265 A., however (41).

In passing it may be pointed out that the quantum yield for pepsin is in the range reported for other proteins, namely 10^{-2} to 10^{-3} (12, 29).

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*It has been pointed out by G. Oster that if this concept is correct, a lower quantum yield would be expected in solutions of higher ionic strengths.

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Synopsis

Quantum yields for the inactivation of crystalline swine pepsin have been determined as a function of pH at 2537 A. The quantum yield is near a minimum at pH 4.08, at which point a value of 0.0019 was found, rises rapidly above pH 6, and shows a slight maximum near pH 2.7. The maximum is more pronounced with polychromatic light. The quantum yield (at pH 2.01) was found to be the same with either hemoglobin or casein as a substrate. Urea had no effect on the quantum yield although urea alone, 7 M, inactivates pepsin at an appreciable rate. Urea and light denaturation do not modify the absorption spectrum of pepsin in the same way. The data of Gates has been recalculated; it shows an increase of quantum yields with decreasing wave length. It has been concluded, from experiments with model substances, that inactivation can occur by the absorption of a quantum by any aromatic group in pepsin.

Résumé

Le rendement quantique de l'inactivation à la raie 2537 A. de la pepsine de porc cristalline a été déterminée en fonction du pH. Ce rendement est proche du minimum au pH 4.08, où une valeur de 0.0019 a été trouvée; il s'accroît rapidement au dessus de pH 6, et il manifeste un maximum faible près de pH 2.7. Le maximum est plus prononcé avec une lumière polychromatique. Le rendement quantique (à pH 2.01) a été trouvé identique aussi bien dans le cas de l'hémoglobine, que de la caséine, comme substrats. L'urée est sans effet sur ce rendement, bien que l'urée seule, 7 M, inactive la pepsine dans une mesure appréciable. La dénaturation à l'urée et la dénaturation à la lumière modifient le spectre d'absorption de la pepsine de façon différente. Les données de Gates ont été recalculées; les rendements quantiques s'accroissent avec des longueurs d'onde décroissantes. On en conclut, à la suite d'expériences sur des substances modèles, que l'inactivation peut se produire par l'absorption d'un quantum par un groupe aromatique, présent dans la pepsine.

Zusammenfassung

Es wird die Quantenausbeute fur die Inaktivierung von krystallisiertem Schweinepepsin als eine Funktion der Wasserstoffionen-Konzentration bei 2537 A. bestimmt. Die Quantenausbeute zeigt ein Minimum bei pH 4.08, steigt rasch ueber pH 6 und zeigt ein schwaches Maximum in der Naehe von pH 2.7. Das Maximum ist mehr ausgesprochen bei der Anwendung von polychromatischem Licht. Die Quantenausbeute (bei pH 2.01) ist die gleiche fur Hemoglobin oder Casein als Substrat. Harnstoff hat keinen Effekt auf die Quantenausbeute, obwohl reiner, 7 M, Harnstoff Pepsin in betraechtlichem Masse inaktiviert. Die Modifikation des Absorptionsspektrums von Pepsin ist nicht die gleiche, wenn die Denaturierung einmal durch Harnstoff und das andere Mal durch Lichteinwirkung erfolgt. Es werden die Werte von Gates nachgerechnet. Sie zeigen ein Anwachsen der Quantenausbeute mit verringerter Wellenlaenge. Aus Versuchen mit Modellesubstanzen wird geschlossen, dass die Inaktivierung erfolgen kann waehrend der Absorption eines Quantums bei jeder der aromatischen Gruppen in Pepsin.

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Adhesion.
III. Adhesion of Polymers to Cellulose and Alumina

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INTRODUCTION

In previous papers (1-4) a number of factors involved in adhesion were demonstrated experimentally. With a series of isoviscous polymers containing a highly polar, hydrogen-bonding group, -COOH, it was shown that the relationship:

$$\text{Adhesion} = k(\text{COOH})^n \qquad (1)$$

holds for adhesion to regenerated cellulose, where n has an average value of 0.59.

The temperature dependence of the adhesion of such materials to cellulose has been interpreted to involve an energetic competition between adsorption of polymer on the substrate and cohesion of the polymer for itself. The heat of adhesion is the sum of a heat of adsorption (exothermic) and a cohesive energy of polymer (endothermic). In other words, there is a specific attraction between polar groups in the cellulose and polar hydrogen-bonding groups in the polymer that involves heats of sorption, and there is a cohesive attraction of the polymer internally that involves an energy of cohesion; some of the energy of cohesion must be supplied in order for polar groups to emerge to the interface (5). The relative magnitudes of these energies determines the influence of temperature on adhesion. If the energy of cohesion is greater than the heat of sorption, adhesion will increase with increasing temperature. The influence of a plasticizer on the magnitude of adhesion has been exemplified.

It is the purpose of this paper to extend the observations to aluminum as a substrate and further to illustrate the role of humidity, molecular weight, tack temperature, and polymer composition on adhesion.

EXPERIMENTAL

Adhesion Measurements

Adhesion measurements and bond formations were performed in a manner similar to that described previously (2,3). Instead of a mechanical heat-sealer, however, an electrically heated plate covered with a smooth sheet of aluminum and a roller were used. The roller was constructed from a ball-bearing wheel, weighing 96 g. and 5/8 in. in width, which was attached to a handle by a universal joint. The handle with a joint was used to insure fairly uniform pressure over the contact area. The joints were prepared by rolling the roller across the lapped films eight times, four each way (3). Sticking of films to the plate was prevented by lubrication with a trace of Silicone stopcock grease. The temperature of the plate was controlled to ±2°C. A hand pyrometer was used to measure surface temperature.

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*From a thesis submitted by C. J. Seiler to the Graduate School of Polytechnic Institute of Brooklyn for the M. S. degree, June, 1948.

Tack temperatures reported here in (except in Table V) were determined with the roller and are not to be compared with results reported elsewhere (4) as determined with a mechanical heat-sealer under specified conditions (3,4).

Joint Failure

It was important to know whether joints broke by adhesion failure between polymers and substrate (a measurement proportional to true adhesion) or by cohesion failure within the polymer (a measurement proportional to tensile strength). The following simple tests were employed to evaluate joint failure. Cellophane joints were examined, after stripping, by immersion in a 1% aqueous solution of fuchsin. Exposed cellulose dyed red; the extent of any incomplete stripping of polymer from substrate was readily discernible (3,4). Aluminum joints were examined visually with a bright light and a magnifying glass, or better, by dipping in 20% caustic for a few seconds. The extent of reaction of caustic with the exposed surface enabled an estimate of the fraction of the bond which failed by stripping. Only the stripping load was considered to be a measure of relative adhesion among polymers. For more details of methods, previous papers in this series may be consulted (1-4).

Copolymers

Vinyl chloride-vinyl acetate-maleic acid copolymers were obtained from the Bakelite Corporation, courtesy of L. R. Whiting. Properties of these materials were listed in Table I.

TABLE I. "Vinylite" Resin VMCH Samples

Sample No.	Run No.	Reference	Analysis			Specific viscosity at 20°C.[a]	Tack temperature, °C.
			Vinyl chloride, %	Vinyl acetate, %	Maleic acid, %		
1	E5-125	D995-6	85.2	10.1	4.7	0.592	143
2	E5-134	D995-27	81.5	10.6	7.9	0.502	147
VMCH	-	-	86	13	1	0.53	120
VYHH-1	-	-	87	13	0	0.53	120

[a] 1.00 g. polymer dissolved in 100 ml. methyl isobutyl ketone.

Vinyl acetate-methyl vinyl ketone (VA-MVK) copolymers were prepared from carefully purified monomers. Polymerization was carried out in bulk, to the extent of 15-30%, with benzoyl peroxide as a catalyst. The conditions are summarized in Table II. The polymers decreased in flexibility with increasing ketone concentration. The composition of the copolymers was determined by analyses for carbon and hydrogen.* The mole fractions of methyl vinyl ketone reportted in Table II were averages of values computed from both the carbon and hydrogen contents.

For coating, polymer solutions containing 10g. polymer in 56.7 g. purified dioxane were prepared. In addition, a solution of equal weights of polymers 87-3 and 87-5 was used to obtain a composition of intermediate carbonyl group concentration.

Styrene-methyl vinyl ketone copolymers were prepared in sealed tubes without a catalyst. Pertinent data are in Table III.

A series of vinyl acetate polymers was obtained from the Bakelite Corporation. Pertinent data are in Table IV. The intrinsic viscosities were supplied by the manufacturer.

Substrates

Regenerated cellulose films were used (3) without glycerol softener. Also employed was a 0.52-mil aluminum foil of high surface luster. Analyses of the foil** gave aluminum 99.61%, maganese 0.012%, silicon 0.014%, iron 0.36%, and traces of magnesium and titanium.

RESULTS AND DISCUSSION

Influence of Molecular Weight on Adhesion

We may take the intrinsic viscosities of polyvinyl acetate polymers in cyclohexanone to be roughly proportional to their molecular weights (see below). Figure 1 shows how adhesion is related to intrinsic viscosities [η] of polymers. Somewhere below a viscosity of

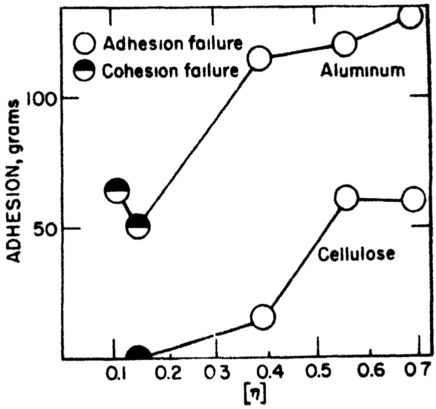

Fig. 1. Adhesion of polyvinyl acetate to cellulose and aluminum versus intrinsic viscosity of the polymers.

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TABLE II. Vinyl Acetate-Methyl Vinyl Ketone Polymers

Expt. No.	Monomer weight, g. Vinyl acetate	Monomer weight, g. Methyl vinyl ketone	Catalyst, %	Reaction temperature °C.	Time, hr.	Degree of polymerization, %	Yield	Mole fraction MVK	Tack temperature °C.
87-1	100	0	0.26	65	2.0	27.2	24.0	0	110
87-2	85	15	0.25	70	5.75	20.1	17.5	0.71	110
87-3	65	35	0.20	70	3.75	24.6	19.6	0.85	110
87-5	35	65	0.20	65	1.75	18.0	14.8	0.95	90
87-6	0	100	0.15	65	1.0	20.0	18.4	1.0	85

TABLE III. Styrene-Methyl Vinyl Ketone Polymers

Expt. No.	Mole fraction MVK	Temperature, °C.	Time, hr.	Mole fraction MVK in polymer	Intrinsic viscosity	Tack temperature, °C.	Film
58-1	0.0	100	9	0.0	0.0115	140	Very flexible
58-2	0.26	100	8	0.26	0.0121	125	Very flexible
58-3	0.40	100	4.5	0.40	0.0121	120	Very flexible
58-4	0.54	100	3.5	0.54	0.0106	110	Flexible
58-5	0.78	100	5.3	0.78	0.0085	95	Flexible
58-7	1.00	45	6.0	1.00	0.0291	85	Brittle

about 0.39, cohesive failure of heat seals occurs. Above this value, adhesive failure occurs and increasing the "molecular weight" does not result in a marked improvement of adhesion. Apparently, provided the chains are long enough to resist slippage, adhesion depends only on intermolecular forces between chain segments and substrates. These forces are independent of chain lengths (1,6). Adhesion to aluminum is higher than adhesion to cellophane at 35% relative humidity.

TABLE IV. Polyvinyl Acetate Polymers

Product	Intrinsic viscosity (cyclohexanone, 20°C.)	Tack temperature, °C.
AYAC	0.11	108
AYAB	0.15	112
AYAA	0.39	115
AYAF	0.56	120
AYAT	0.69	125

Tack Temperature and Molecular Weight

Tack temperature has been defined as that temperature at which the melt viscosity becomes low enough for two thin slabs of polymer to merge at an arbitrary pressure and in a given time. It was assumed previously and is further assumed here that under the same experimental conditions all polymers have equal viscosities at their respective tack temperatures. For two related materials we may write (7):

$$\ln \eta_1 = \ln \eta_2 = A_1 + CM_1^{1/2} + B/T_1 = A_2 - CM_2^{1/2} + BT_2 \qquad (2)$$

Here, η is melt viscosity, M is average molecular weight, T is absolute temperature, and A, B, and C are constants characteristic of the series. From this equation we have a way of predicting a tack temperature T_2 if T_1, M_1, and M_2 are known. The well-known Staudinger equation, as modified by Mark et al. (8) may be written for the intrinsic viscosity $[\eta]$ as;

$$[\eta] = KM^a \qquad (3)$$

Substitution of equation 3 into 2 gives:

$$\ln \eta = A_1 + C'[\eta]_1^{1/2a} + B/T_1 = A_2 + C'[\eta]_2^{1/2a} + B/T_2 = \ldots \qquad (4)$$

and for a given melt viscosity we have:

$$[\eta]^{1/2a} = K' - B'/T \qquad (5)$$

where K′ and B′ are new constants for the conditions extant. Thus a plot of $[\eta]^{1/2a}$ against the reciprocal of the absolute temperature for a series of chemically identical polymers would expectedly give a straight line, provided the exponent in equation 2 is one-half.* Using the value of a = 0.67 as an approximation (9), we have prepared this plot (Fig. 2). The data approximates a straight line. Unfortunately the tack temperatures were not determined with an accuracy of more than ±2°C. and the exponent of M is not known at present and may differ from 1/2. These results only serve to illustrate the meaning of tack temperature for polymers. Tack temperature is considerably more sensitive to variations in chemical composition than to variations in molecular weight. It has been found to vary from below 0°C. to above 200°C. for miscellaneous polymers previously conditioned to 35% relative humidity (4).

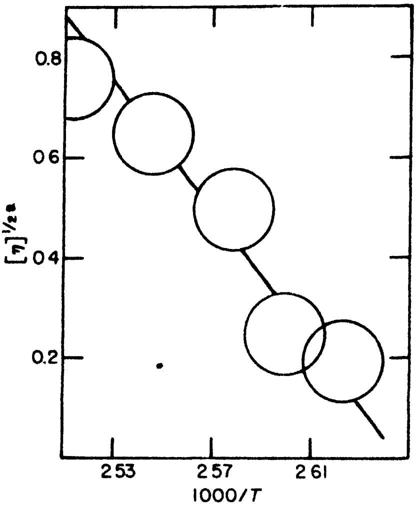

Fig. 2. Intrinsic viscosity-tack temperature relationship for polyvinyl acetate.

Influence of Solvent on Adhesion

No difference in adhesion of polyvinyl acetate on cellulose or aluminum was noted with dioxane, acetone, or carbon tetrachloride as a solvent. With acetone-water as a solvent, however, as the concentration of water was increased from 0 to 3.45% based on weight of the polymer, adhesion of the dried, heat-sealed films approached a maximum toward aluminum (Fig. 3). Further additions of water in the solvent used in preparing the coatings led to a decrease in adhesion. This may be explained by the fact that the addition of a highly polar solvent such as water permits the polar groups of the polymer to attain closer proximity to the surfaces by virtue of an improved wetting action. The addition of higher proportions of water, however, has an insolubilizing effect on the polymer, causing a "balling up" of the molecules (10). This may lead to a poorer wetting of the surface. No such maximum in adhesion was observed with cellulose as a substrate.

*P. J. Flory has since shown that the exponent is not one-half for all polymers. Symposium on Military Aspects of Colloids, Edgewood Arsenal, June 28-29, 1948.

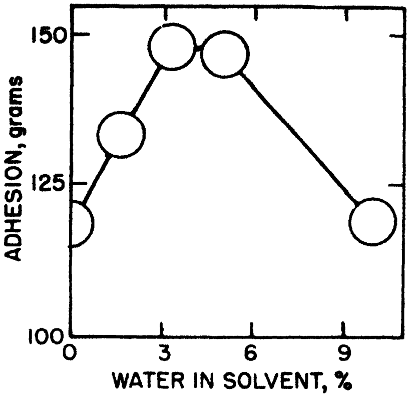

Fig. 3. Adhesion of polyvinyl acetate to aluminum as a function of amount of water in water-acetone solvent used during coating operation.

Influence of Humidity on Adhesion

From Figure 4 it may be concluded that low humidity tends to improve the adhesion of the more hydrophobic polymers (those high in styrene) to cellulose, whereas the adhesion of the polar polymer from polymethyl vinyl ketone is slightly improved at the higher humidity. Polyvinyl acetate gave an adhesion of 43 g. per linear 1.5 in. at 70% relative humidity, and 29 g. at 35% relative humidity (R.H.). These phenomena are probably associated partly with an elution effect in the sorption of the polymer on the substrate (1), and partly with a plasticization of the polymer (4). These points have been discussed previously. It may be speculated that, with the former effect predominating, adhesion would be lessened at higher humidity and, with the latter factor predominating, adhesion would be improved at higher humidity. Similar findings have been reported by De Bruyne (11) and others (12-14).

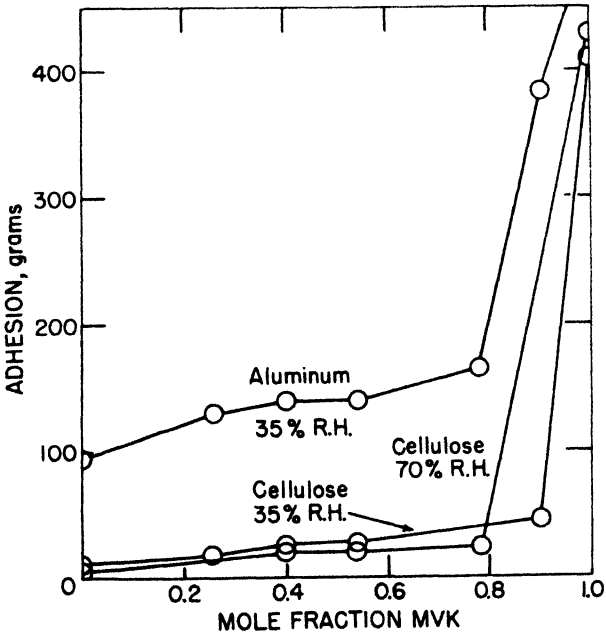

Fig. 4. Adhesion of styrene-methyl vinyl ketone copolymers to cellulose and aluminum.

Influence of Polymer Composition on Adhesion

It has been shown that provided all members of a series of polymers have the same tack temperatures, adhesion to cellulose may be expressed by an equation, 1, where the concentration of polar groups is raised to a fractional power. This is true for vinyl chloride-vinyl acetate-maleic acid copolymers, or mixtures of such a polymer with vinyl chloride-vinyl acetate polymer, and for ethylene-vinyl alcohol polymers. This interesting relationship is approximated at low maleic acid concentrations with aluminum as a substrate, i.e., below a mole fraction of 0.012–0.016 (3–4%) (see Fig. 5). At higher maleic acid concentrations, adhesion passes through a maximum. Falling off in adhesion to aluminum of the maleic acid copolymers containing more than 3.7% of maleic acid is probably due to excessive corrosion of the aluminum (15).

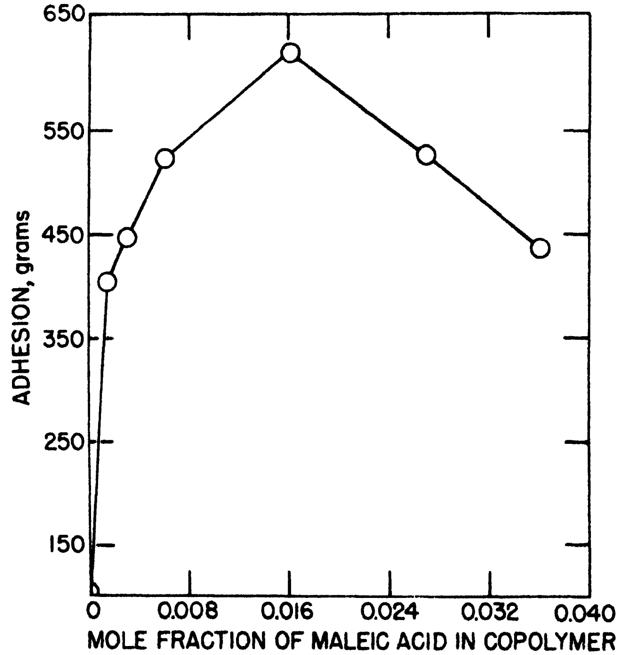

Fig. 5. Adhesion of vinyl chloride-vinyl acetate-maleic acid copolymers to aluminum.

Copolymers of styrene and methyl vinyl ketone and of vinyl acetate and methyl vinyl ketone both show a gradual increase in adhesion to cellophane and aluminum with increasing carbonyl concentration up to 0.8 mole fraction of ketone — Figure 4 and 6. Above this point, adhesion increases rapidly. These copolymers show a pronounced decrease in tack temperature (Tables II and III), with increasing ketone concentration. It is probable that two important factors contribute to relatively high adhesion at high ketone concentrations. One may speculate that below 0.8 mole fraction of ketone (MVK) the material behaves as an aromatic hydrocarbon polymer in that the molecules have their nonpolar portions "outside" and exhibit properties like those displayed by long-chain alcohols in solution (16). At higher ketone concentrations there is a "reversal of phase" and the polar portion of the molecules are "outside" and are available for adhesion (1). More important, perhaps, is the fact that above 0.8 mole fraction, tack temperature of the members of both series have fallen into the region of adhesion as demonstrated previously for high polymers (4), (Tables II and III). This improved adhesion is probably partly attributable to a reduction in "cohesive energy density" (2-4), argument for improved flexibility is not substantiated by data of Table III.

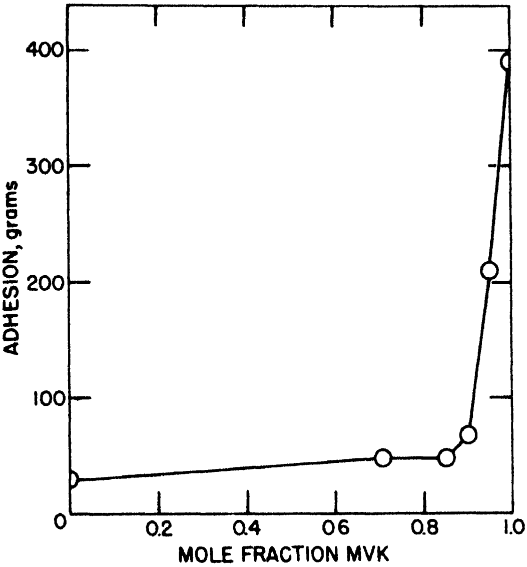

Fig. 6. Adhesion of vinyl acetate-methyl vinyl ketone copolymers to cellulose.

The adhesion of a series of ethylene-vinyl chloride (E-VCl) copolymers to cellulose (4) progresses similarly to the MVK copolymers (4), (Table V). As the tack temperature dropped from 90-100°C. to 25°C., adhesion increased from about 0 to nearly 1000 g. Adhesion was considerably improved by adding a plasticizer or by increasing the temperature of heat-sealing (1). For this series, log viscosity of the polymer solution (Table V) was proportional to tack temperature. For these polymers, tack temperatures are lower than for polyethylene or polyvinyl chloride. Neither polyethylene or polyvinyl chloride show adhesion to cellulose.

Influence of Temperature on Adhesion

In general, as temperature increases, so does adhesion of polymers to cellulose. Eventually, however, the temperature is high enough to allow for rapid viscous flow and a marked reduction in tensile strength of polymers. At the higher temperatures, heat-seal bond failure results from cohesive failure within the polymer rather than from interfacial stripping. This is illustrated in Figure 7 wherein cohesion failure at higher temperatures together with increasing adhesion is responsible for the maximum in bond strengths observed (data from reference 3).

TABLE V. Adhesion of Vinyl Chloride-Ethylene Polymers to Cellulose

VCl/E mole ratio	Viscosities, poises [a]	Tack temperature, °C.	Adhesion
0:1	-	105	0
1.1:1	-	<25	1275
1.95:1	0.34	~25	850
3:1	0.9	58	60
4.5:1	2.5	89	60
12:1	3.4	98	50
1:0	-	106	~0

[a] 10% solutions in cyclohexanone.

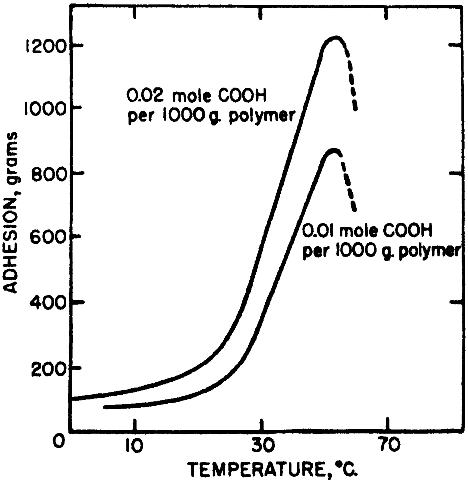

Fig. 7. Adhesion of polymers to cellulose as a function of temperature. Dotted line indicates cohesive failure.

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Synopsis

A relationship between tack temperature and molecular weight has been deduced and illustrated with polyvinyl acetate polymers. Provided the molecular weight is high enough to prevent cohesive failure, the adhesion of polyvinyl acetate to cellulose and aluminum is independent of molecular weight. The influence of humidity on adhesion of polymers to cellulose is shown. The influence of polymer composition on adhesion is illustrated with copolymers of vinyl acetate and methyl vinyl ketone and with styrene and methyl vinyl ketone. Above a mole fraction of ketone of 0.8, adhesion increases rapidly. The interdependence of tack temperature and composition on adhesion is exemplified with ethylene - vinyl chloride copolymers. A temperature dependence of adhesion is cited for copolymers containing maleic acid.

Résumé

Une relation entre la température de recouvrement et le poids moléculaire a été déduite, et illustrée au moyen de polymères à base d'acétate de polyvinyle. Pourvu que le poids moléculaire soit suffisamment élevé pour éviter un manque de cohésion, l'adhésion de l'acétate de polyvinyle à la cellulose et l'aluminium est indépendante du poids moléculaire. L'influence de l'humidité sur l'adhésion des polymères à la cellulose est mise en évidence. L'influence de la composition du polymère sur l'adhésion est illustrée au moyen de copolymères d'acétate de vinyle et de méthylvinylcétone, et de styrol

et de methylvinylcétone. Aus dessus d'une fraction molaire en cétone de 0.8 l'adhésion s'accroît rapidement. La dépendance de la température de recouvrement et de la composition sur l'adhésion est illustrée par des copolymères éthylène-chlorure de vinyle. La dependance thermique de l'adhésion est indiquée pour des copolymères à base d'acide maléique.

Zusammenfassung

Es wird eine Beziehung zwischen Klebetemperatur und Molekulargewicht für Polyvinylazetät-Polymere abgeleitet. Die Adhäsion von Polyvinylazetat an Cellulose und Aluminium ist unabhängig vom Molekulargewicht, vorausgesetzt dass das Molekulargewicht hoch genug ist, um Kohäsionszusammenbruch zu verhindern. Der Einfluss der Feuchtigkeit auf die Adhäsion von Polymeren an Cellulose wird nachgewiesen. Der Einfluss der Polymerzusammensetzung auf die Adhäsion wird für Mischpolymeren von Methylazetat in Methylvinylketonen und mit Styrol in Methylvinyketone illustriert. Die adhäsion nimmt stark zu oberhalb eines Molenbruches von Keton von 0.8. Der Zusammenhang zwischen Klebetemperatur und Zusammensetzung und ihr Einfluss auf die Adhasion wird für Äthylenvinylchlorid Mischpolymere beschrieben. Für Mischpolymere, die Maleinsäure enthalten, wird eine Temperaturabhängigkeit der Adhäsion festgestellt.

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Photochemistry of Phosphonitrilic Chlorides. I. A Photochemical Reaction of Low-Polymeric Phosphonitrilic Chlorides

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INTRODUCTION

Phosphonitrilic chlorides, first obtained by Liebig (1) in 1834, have aroused enthusiasm in a great number of investigators because of their unusually interesting properties. Much work has been done in the field of phosphonitrilic chlorides since they were first synthesized. A great number of papers have been published in which the structures and the physical, chemical, and polymeric properties have been recorded (2,3). However, there have been no reports until now about the changes these compounds can undergo when they are irradiated with ultraviolet light.

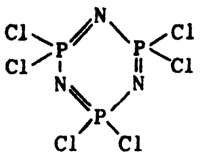
In the course of an investigation of the fluorescence spectra of polymeric phosphonitrilic chloride, we observed some interesting changes in these compounds which led us to undertake a thorough study of the photochemistry of the entire group of phosphonitrilic chlorides. The present paper deals only with a photochemical reaction that takes place when trimeric or tetrameric phosphonitrilic chlorides dissolved in nonpolar organic solvents are exposed to ultraviolet light.

Due to the sudden tragic death of our colleague, Dr. B. R. Dishon, it was deemed fitting to publish these preliminary results now in honor of his memory.

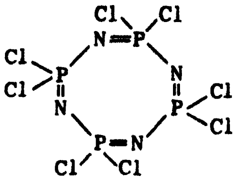
EXPERIMENTAL

The trimer (I) and the tetramer (II) were prepared according to Schenck and Roemer (4) from phosphorus pentachloride and ammonium chloride in tetrachloroethane. Both were purified by recrystallization from low-boiling petroleum ether and by repeated fractional distillation. The trimer was collected at 127°C. (13 mm.) and the tetramer at 199.5° (27 mm.). The trimer crystallizes in six-sided plates belonging to the rhombic system (5,6), and has a melting point of 114°C. The tetramer crystallizes in the tetragonal system (7,8) and ist melting point is 123.5°C. If a sample, sealed under high vacuum in a Pyrex tube, polymerized at 300°C. with no color changes, it was considered pure for our purposes. In our experiments only freshly distilled samples were used.

X-ray studies (7-9) point to the fact that both the trimer (I) and the tetramer (II) possess cyclic structures with alternate phosphorus and nitrogen atoms, whereas the higher members possess chain structures:



(I)



(II)

The solvents were purified by the standard methods used for preparing spectroscopically pure materials (10). The following solvents were used: hexane, benzene, toluene, and decahydronaphthalene.

Two types of mercury lamps were employed as irradiating sources. One was a water-cooled, vertical mercury arc surrounded concentrically by two reaction vessels-similar to the one used in previous investigations (11). Some improvement in the construction of the lamp, however, has been made, as shown in Figure 1. This lamp was operated at 2200 watts d.c. and was situated approximately 2 cm. from the reaction vessel. The latter had a capacity of 190 cc.

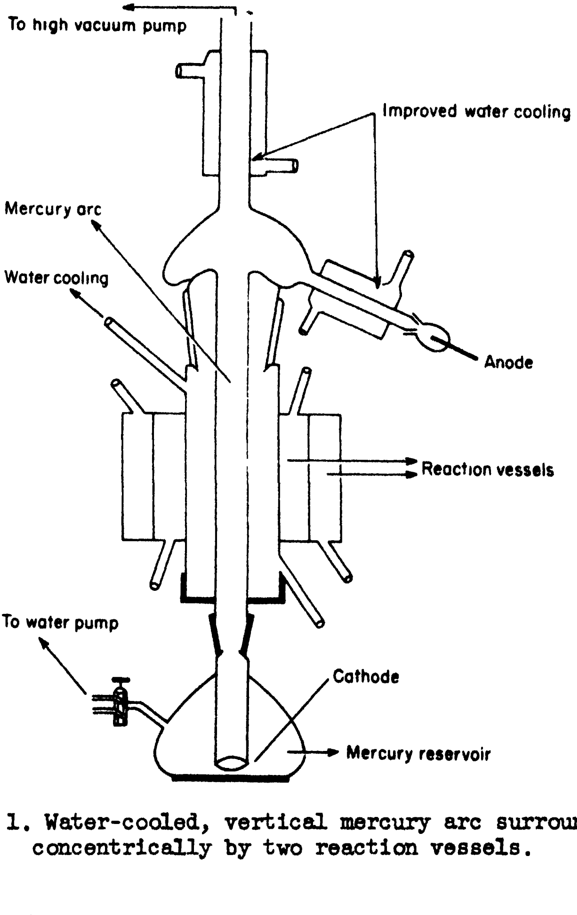


Fig. 1. Water-cooled, vertical mercury arc surrounded concentrically by two reaction vessels.

The second was a high-pressure, air-cooled mercury arc operating also on d.c. (660 watts) and inclined slightly to the horizontal. When this light source was used, the reaction vessel employed was a round quartz cell 10 cm. long with parallel walls of 2.5-cm. diameter. The distance between the cell and the arc during irradiation was about 8 cm. This arrangement was used especially when homogeneous films of trimeric or tetrameric phosphonitrilic chloride were irradiated. These films were prepared on the inside walls of the quartz cell and were closed under vacuum. The above method was also used for continuous irradiation of the insoluble photoreaction products formed from solutions of the trimer or tetramer.

The radiation tubes and reaction vessels used in this investigation were made from very pure transparent quartz.

EXPERIMENTAL RESULTS AND DISCUSSION

Homogeneous films of trimeric or tetrameric phosphonitrilic chlorides remained stable after a continuous irradiation for 40 hours with the full mercury arc. However, solutions of these compounds, which were initially colorless, gradually became brown on irradiating under the same conditions, and gelatinous deposits were formed on the walls of the reaction vessel.

Qualitatively, the effect is the same in hexane, benzene, toluene, and decahydronaphthalene.

The gradual formation of the brown deposit made it preferable to irradiate the solution only for short periods, to isolate the photoproducts, and to recirculate the unchanged starting material. Alternatively, one can work in dilute solution, in order to increase the conversion (Fig. 2). The rates of reaction are given in Table I.

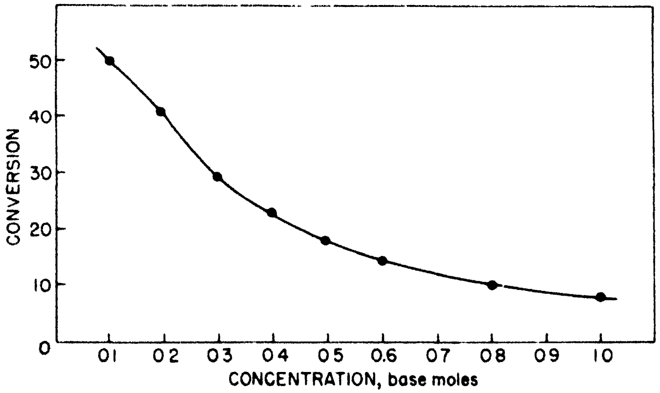


Fig. 2. Conversion percentage versus concentration for $(NPCl_2)_3$ in benzene per five hours irradiation.

Both soluble and insoluble photoreaction products are formed. The soluble products consisted of distillable, almost colorless liquids, and nondistillable brown substances which polymerize on heating. The former could be separated by fractional distillation into several fractions, as indicated in Table II.

TABLE I. Rate of photoreaction of Phosphonitrilic Chloride Using 2200 Watt Mercury Lamp

Starting material	Solvent	Concentration, base moles*	Irradiation time, hrs.	Conversion, %**
$(PNCl_2)_3$	Benzene	0.5	15	30
	Benzene	0.1	5	50
	Decahydro-naphthalene	0.5	15	58
	Decahydro-naphthalene	0.1	5	75
$(PNCl_2)_4$	Benzene	0.5	15	26
	Decahydro-naphthalene	0.5	15	42

---

*Based on $PNCl_2$.

**Calculated from quantity of starting material recovered.

The gelatinous brown deposits are insoluble in organic solvents–swelling only in some of them; they resist the attack of a hot mixture of chromic and sulfuric acids, and are destroyed only by boiling with concentrated nitric acid. The best method of isolating them is by mechanical agitation of the reaction vessel with organic liquids or with water, which serves to detach the deposit from the walls in the form of transparent lamellae.

TABLE II. Soluble Photoreaction Products

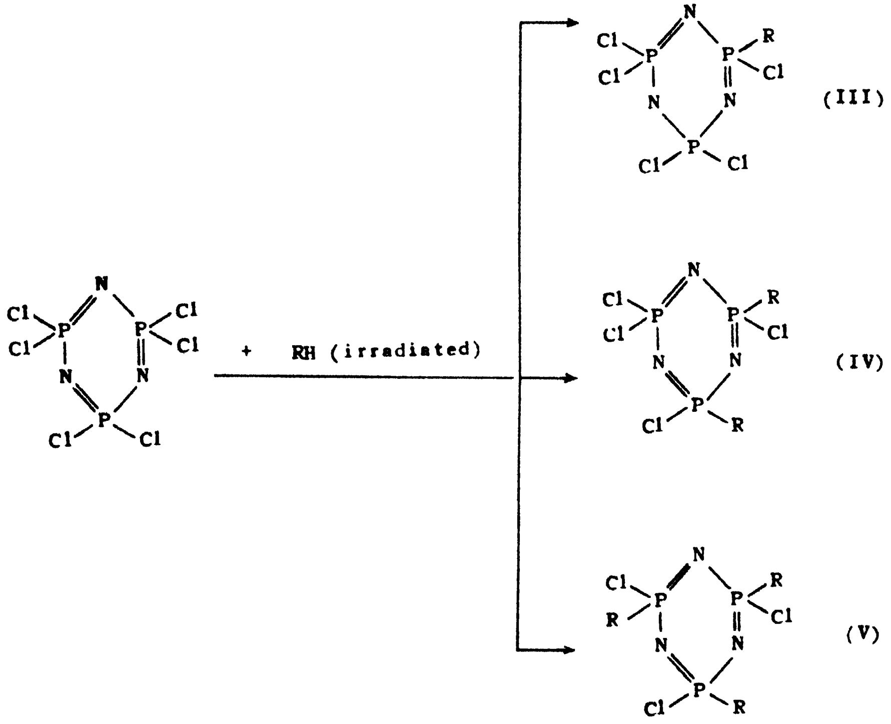
Starting material	Boiling range	Fractions isolated
$(PNCl_2)_3$ in benzene	154°-180° C. (0.25 mm.)	(a) 123°C.(0.025 mm.) (b) 123-127°C.(0.025 mm.) (c) 127-133°C.(0.06 mm.)
$(PNCl_2)_3$ in decahydro-naphthalene	159-181°C. (0.15 mm.)	(d) 133-138°C.(0.03 mm.) (e) 138-144°C.(0.03 mm.) (f) 144-149°C.(0.03 mm.) (g) 153-180°C.(0.03 mm.)
$(PNCl_2)_4$ in decahydro-naphthalene	180-185°C. (0.05 mm.)	(h) 180-185°C.(0.05 mm.)

Our first assumption was that photopolymerization of the phosphonitrilic chlorides had taken place. There was no increase in the viscosity of the irradiated solution compared with that of the starting solution, and therefore, no appreciable amount of soluble polymer could have been present. However, it was still possible that the assumed polymerization led at once to the highly polymerized, insoluble phosphonitrilic chlorides.

In order to check this assumption, the chlorine content of the insoluble photoproduct was determined. Chlorine is known to be split off readily from low- as well as high-polymeric phosphonitrilic chlorides by hydrolysis with water in the presence of pyridine. The insoluble photoproduct was refluxed for 6 hours with a pyridine–water mixture, and then analyzed for its chlorine content. The photoproduct contained only 17.4% chlorine instead of the expected 61.1%. The photoproduct cannot therefore be polymeric phosphonitrilic chloride.

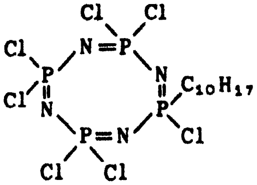
The next assumption was that the solvent participates in the photochemical reaction. We had therefore to analyze each isolated reaction product for its carbon and hydrogen content. The analyses of the soluble photoproducts showed that successive substitution of the chlorine atoms by the radicals, R, of the solvent, RH, had taken place (see Table III).

The photochemical reaction of trimeric phosphinitrilic chloride, therefore, can be represented schematically as follows:



The indicated distribution of substituents in (IV) and (V) is, of course, arbitrary.

Although, in the case of the tetramer, we could only isolate a substance which probably has the structure (VI), the photochemical reaction of the tetramer seems to follow the same course as that of the trimer:



(VI)

The soluble, but not distillable, brown reaction products are transformed at about 200°C. into brown amorphous substances, still soluble in benzene but no longer soluble in hexane. At higher temperatures they are changed into a glossy-black, hard, brittle resin, insoluble in the usual organic solvents. These substances contain a high percentage of hydrogen and carbon and are therefore derived from the starting material by stepwise replacement of the halogen atoms by organic radicals.

TABLE III. Carbon and Hydrogen Content of Fractionated Photoreaction Products.

Starting material	Solvent (RH)	Fraction	Carbon, %	Hydrogen, %
$(PNCl_2)_3$	Benzene	(a)	21.1	2.5
		(b)*	20.1	1.8
		(c)	23.7	2.8
	Decahydronaphthalene	(d)**	55.3	8.3
		(e)***	45.7	6.1
		(f)	41.6	5.8
		(g)	39.6	5.8
$(PNCl_2)_4$	Decahydronapthalene	(h)****	23.1	4.1

*Fraction (b) calculated for $P_3N_3Cl_5 \cdot C_6H_5$: C, 18.5%; H, 1.3%

**Fraction (d) calculated for $P_3N_3Cl_3.(C_{10}H_{17})_3$: C, 55.2%; H, 7.9%.

***Fraction (e) calculated for $P_3N_3Cl_4.(C_{10}H_{17})_2$: C, 43.6%; H, 6.2%.

****Fraction (h) calculated for $P_4N_4Cl_4.C_{10}H_{17}$: C, 21.3%; H, 3.0%.

Table IV shows that the insoluble photoreaction deposits also contain carbon and hydrogen, although no definite formulas can be ascribed to them.

TABLE IV. Carbon and Hydrogen Content of Insoluble Photoreaction Products

Starting material	C, %	H, %
$(PNCl_2)_3$, in benzene	33.2	6.0
$(PNCl_2)_3$, in decahydronaphthalene. . .	35.2	4.8
$(PNCl_2)_4$, in benzene	38.7	7.7
$(PNCl_2)_4$, in decahydronaphthalene. . .	47.1	9.6

It is interesting to note that continued irradiation of a suspension of the deposit in benzene leads to a progressive loss of chlorine (Fig. 3).

Decahydronaphthalene is more reactive than benzene, as would be expected from the C-H bond energies in the two hydrocarbons (12); trimeric phosphonitrilic chloride (I) appears more reactive than the tetramer (II).

The substitution reaction leading to the colorless liquid compounds is neither preceded nor accompanied by an opening of the rings in (I) and (II) -as otherwise a whole range of polymers should have formed and the same products should have been obtained from both (I) and (II), which is not the case. There is no interconversion of the trimer and tetramer. Obviously, the rings (I) and (II) are quite stable, and in this respect resemble the systems of benzene and cyclooctatetraene, respectively. The main difference lies in the strength of the bond leading from the ring to the halogen atoms-a point which we shall endeavor to investigate quantitatively.

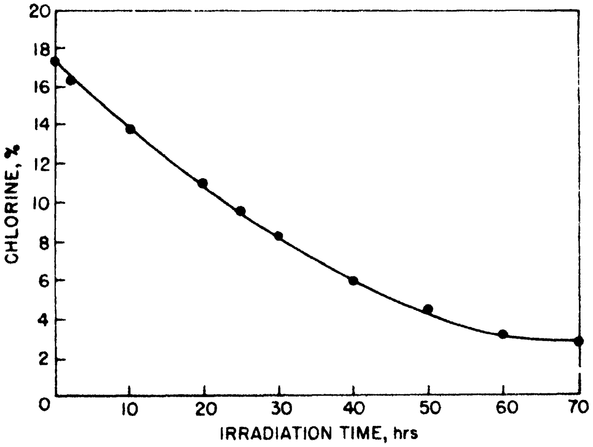


Fig. 3. Decrease in chlorine content of the deposit by continuous irradiation in benzene.

In view of the fact that phosphonitrilic chloride is an acid chloride, this reaction is analogous to the substitution of hydrocarbons by phosgene and oxalyl chloride, which Kharasch and his school have studied (13).

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Synopsis

Photochemical reactions of trimeric and tetrameric phosphonitrilic chlorides with some hydrocarbons are described. Soluble and insoluble photoreaction products are formed. From the soluble fraction, distillable phenyl- and decahydronaphthyl-phosphonitrilic chlorides were separated; the indistillable and deposit fractions were also found to contain high percentages of carbon and hydrogen. This shows that successive substitution of the chlorine atoms by radicals, R, of the solvents, R-H, had taken place.

Résumé

Les réactions photochimiques des chlorures de phosphonitriles, trimères ou tétramères, avec certains hydrocarbures sont décrites; les produits de réaction sont partiellement solubles. Da la fraction soluble, on isole par distillation des chlorures de phenyl- et de decalyl-phosphonitriles; egalement le résidu de distillation et la fraction insoluble contiennent un pourcentage élevé en carbone et en hydrogène. Ceci démontre qu'il y a une substitution progressive des atomes de chlore par les radicaux R des solvants, symbolisés par R-H.

Zusammenfassung

Es werden photochemische Reaktionen von trimeren und tetrameren Phosphornitrilchloriden und Kohlenwasserstoffen beschrieben. Lösliche und unlösliche Reaktionsprodukte bilden sich. Aus den löslichen Fraktionen werden destillierbare Phenyl- and Dekahydronaphthyl-phosphornitrilchloride isoliert: auch die nicht destillierbaren und Bodensatzfraktionen enthalten einen höheren Prozentsatz an Kohlenstoff und Wasserstoff. Dies beweist, dass eine stufenweise Substitution der Chloratome durch Radikale R des Lösungsmittels R-H stattgefunden hat.

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Methods for Estimating Intrinsic Viscosity

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There have been proposed so many equations (1) connecting the dilute solution viscosity of high polymers with the concentration that the description of other relationships having no particular advantages would be without value. However, there are a number of viscosity functions which have the important property that for many polymer solutions their numerical value is almost independent of concentration; hence, a good estimate of intrinsic viscosity can be obtained from one measurement of relative viscosity at a convenient concentration. These equations may be derived from the power series expansion of viscosity versus concentration, to which Huggins' (1a) equation:*

$$\eta_{sp} = [\eta]c + k'([\eta]c)^2 \tag{1}$$

is a second-order approximation. Some of these functions** are:

$$\varphi_1 = \frac{1}{c}(2\eta_{sp} - 2 \ln \eta_r)^{1/2} = [\eta] + (k' - 1/3)[\eta]^2 c + \ldots \tag{2}$$

$$\varphi_2 = \frac{1}{4}\frac{\eta_{sp}}{c} + \frac{3}{4}\frac{\ln \eta_r}{c} = [\eta] + (k' - 3/8)[\eta]^2 c + \ldots \tag{3}$$

$$\varphi_3 = \frac{1}{3}\frac{\eta_{sp}}{c} + \frac{2}{3}\frac{\ln \eta_r}{c} = [\eta] + (k' - 1/3)[\eta]^2 c + \ldots \tag{4}$$

$$\varphi_4 = \frac{\eta_{sp}}{c} e^{-\eta_{sp}/3} = [\eta] + (k' - 1/3)[\eta]^2 c + \ldots \tag{5}$$

$$\varphi_5 = \frac{(1 + 1.5\eta_{sp})^{1/2} - 1}{0.75c} = [\eta] + (k' - 3/8)[\eta]^2 c + \ldots \tag{6}$$

---

*Following the usual terminology,

η_r = relative viscosity
η_{sp} = specific viscosity = $\eta_r - 1$
$[\eta]$ = intrinsic viscosity
$= \lim_{c \to 0} \frac{\eta_{sp}}{c} = \lim_{c \to 0} \frac{\ln \eta_r}{c}$
c = concentration
k′ = slope constant

**The author is indebtedto W. H. Stockmayer for suggesting of some these functions.

$$\varphi_6 = \frac{(1 + 4/3\eta_{sp})^{1/2} - 1}{0.67\,c} = [\eta] + (k' - 1/3)[\eta]^2 c + \ldots \qquad (7)$$

$$\varphi_7 = \frac{4}{c}(\eta_r^{1/4} - 1) = [\eta] + (k' - 3/8)[\eta]^2 c + \ldots \qquad (8)$$

$$\varphi_8 = \frac{3}{c}(\eta r^{1/3} - 1) = [\eta] + (k' - 1/3)[\eta]^2 c + \ldots \qquad (9)$$

The functions ϕ_1, ϕ_2, and ϕ_3 are derived form the expansion of ln η_r, and ϕ_4 from a corresponding exponential expansion. ϕ_5 and ϕ_6 are obtained from the quadratic solutions of Huggins' equation, whose positive root is:

$$\varphi_9 = \frac{(1 + 4k'\eta_{sp})^{1/2} - 1}{2k'\,c} \qquad (10)$$

ϕ_7 and ϕ_8 are derived from Philipoff's equation (1):

$$\eta_r = \left(1 + \frac{[\eta]\,c}{n}\right)^n \qquad (11)$$

where n is a positive number. The derivations are straightforward and neglect terms with powers of c higher than the second.

The usefulness of these equations arises from the fact that, for many polymer-solvent systems, k′ is not far from 1/3 or 3/8, and the second term on the right-hand side becomes very small. The particular equation which fits the data best depends on the value of k′ and the behavior of the higher order terms which have been neglected in obtaining ϕ_1 to ϕ_8. Similarly, the behavior on extrapolation to $c = o$ (to obtain the intrinsic viscosity) of ϕ_1 to ϕ_8, η_{sp}/c and ln η_r/c will depend on the higher terms, and the function giving the best straight line may have to be selected by experience. If k′ is not near 1/3 or 3/8, other functions similarly derived may prove more useful.

Gregg and Mayo (2) have used ϕ_5 to estimate the intrinsic viscosities of solutions of polystyrene in benzene. Certain of these functions are now being used in this laboratory to estimate the intrinsic viscosity of polymethyl methacrylates in ethylene dichloride from a single measurement at a concentration chosen so that η_{sp} is near 0.3. For this system, k′ is near 1/3. Table I shows a few sets of data selected at random from our files to test the equations.

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TABLE I. Viscosity Data for Polymethyl Methacrylate in Ethylene Dichloride

Polymer designation	$[\eta]$	c, g./100 cc.	η_{sp}/c	$\ln \eta_r/c$	φ_1	φ_3	φ_4	φ_6	φ_8
M_n	0.533	1.060	0.626	0.480	0.524	0.529	0.503	0.528	0.524
		0.530	0.575	0.498	0.525	0.524	0.518	0.528	0.526
		0.265	0.555	0.518	0.530	0.531	0.527	0.529	0.539
		0.133	0.545	0.527	0.532	0.533	0.532	0.533	0.537
M	1.020	1.070	1.380	0.845	0.995	1.024	0.844	1.012	0.988
		0.535	1.198	0.925	1.008	1.016	0.965	1.014	1.006
		0.268	1.110	0.972	1.016	1.018	1.005	1.019	1.018
		0.134	1.068	0.997	1.020	1.021	1.018	1.021	1.020
M_4	0.600	1.040	0.721	0.539	0.593	0.600	0.562	0.597	0.591
		0.520	0.658	0.566	0.595	0.597	0.592	0.595	0.595
		0.260	0.630	0.583	0.598	0.601	0.596	0.602	0.594
M_6	0.400	1.060	0.461	0.375	0.401	0.404	0.392	0.400	0.402
		0.530	0.431	0.388	0.401	0.403	0.399	0.402	0.402
		0.265	0.415	0.393	0.400	0.400	0.400	0.401	0.408
200M	3.77	0.1070	4.29	3.54	3.77	3.79	3.68	3.78	3.76
		0.0803	4.16	3.59	3.77	3.78	3.72	3.78	3.76
		0.0535	4.03	3.65	3.77	3.77	3.75	3.78	3.78
		0.0267	3.89	3.70	3.77	3.77	3.76	3.78	3.78
460M	5.85	0.1450	7.73	5.18	5.92	6.04	5.32	5.98	5.89
		0.0966	7.15	5.45	5.90	6.02	5.68	5.98	5.95
		0.0483	6.44	5.60	5.87	5.88	5.80	5.89	5.86

Synopsis

A number of equations are suggested for estimating intrinsic viscosity from one measurement of relative viscosity at a convenient concentration. Experimental data illustrate the validity of the equations.

Résumé

De nombreuses équations sont proposées pour estimer la viscosité intrinsèque au départ d'une seule mesure de la viscosité relative, à une concentration appropriée. Les résultats expérimentaux illustrent la validité des équations.

Zusammenfassung

Es werden eine Reihe von Gleichungen für die Berechnung der Viskositätszahl aus einer Messung der relativen Viskosität bei einer leicht zugänglichen Konzentration vorgeschlagen. Experimentelle Werte demonstrieren die Anwendbarkeit dieser Gleichungen.

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Stress-Strain Characteristics of Guaran Triacetate*

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INTRODUCTION

Recent work indicates (1,2,3) that guaran, the principal polysaccharide of the endosperm of guar seed, consists predominantly of a chain of mannose anhydride units one-half of which bear a galactopyranoside side chain. A molecule of this general configuration has not heretofore been readily available for examination as to its film properties. Linear polysaccharide molecules such as cellulose and more recently amylose (4,5) have been carefully examined in film form. Acetates of both of these polysaccharides produce strong, pliable films. Amylopectin, a polysaccharide possessing long branches, has also been examined and its acetates are found capable of producing only a highly brittle film, which is not self-supporting. Similar properties are observed among many of the synthetic polymers. Since guaran is a molecule with numerous short branches, its structure lies between that of cellulose and amylose on one hand and amylopectin on the other as illustrated in Figure 1. Consequently, it is of interest to examine the stress-strain curve of guaran triacetate and to compare the tensile strength and elongation at break with values obtained with cellulose triacetate and amylose triacetate films under similar conditions. The results are shown in Figure 2 and Table I. From these data it is apparent that short branches in the neighborhood of one glycosidic unit in length do not adversely affect the film-forming properties of polysaccharide acetates. When guaran triacetate film is plasticized and elongated the molecules orient under plastic flow as indicated by the stress-strain curves and by the fact that the films can, under certain conditions, be elongated up to 550%, whereupon they become anisotropic to polarized light (2) and when broken shatter in lines parallel to the direction of elongation. Because of the side groups, however, the films on elongation do not develop crystallinity which can be detected by x-ray examination (2).

EXPERIMENTAL

Preparation of Guaran Triacetate. Guaran, prepared by the method of Heyne and Whistler (2), i.e., by extraction of guar flour with water and subsequent precipitation with ethanol, is a white, fibrous polysaccharide. Guaran was acetylated by stirring with approximately 33 parts of pyridine and 33 parts of acetic anhydride at 105°C. for 4 hours. The acetate was precipitated by pouring the clear solution into excess ethanol stirred in a Waring Blendor. After repeated washing with ethanol, the product was air-dried. It was white and fibrous resembling in appearance the triacetates of cellulose and amylose. Its acetyl content was found to be 44.8%, while the calculated value for the triacetate is 44.78%.

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*Journal Paper No. 366 of the Purdue University Agricultural Experiment Station, Lafayette, Indiana.

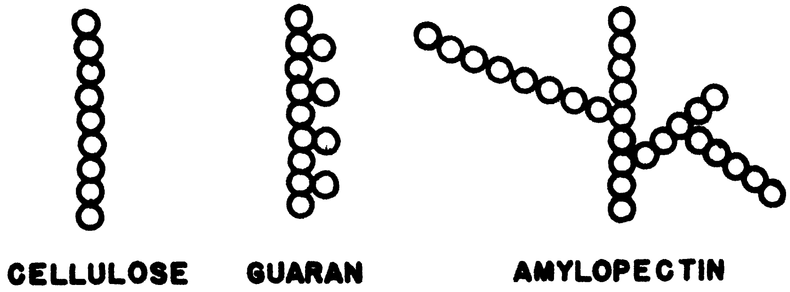

Fig. 1. Diagramatic representation of chain sections from cellulose, guaran, and amylopectin molecules. (O = 1 anhydro sugar unit.)

Preparation of Films. Two grams of guaran triacetate was dissolved in 50 ml. chloroform, and the solution was freed from dust and lint by passage through coarse fritted glass. The solution was concentrated at 70-75°C. in a glycerol bath and, in those cases where plasticized films were to be prepared, a weighed amount of dibutyl tartrate was mixed with the thickened solutions. After concentrating to a 12% solution, the viscous liquid was allowed to stand for several minutes to become free of bubbles and was cast on a clean glass plate with a casting knife having its blade set 0.02 in. above the glass plate. In about 4 hours, the film was carefully loosened by moistening the edges with water and stripped from the plate. After blotting between filter paper, the clear film was cut into strips, dried first in a 60° air oven for 2 hours, and then in a vacuum desiccator overnight. Finally, the strips of film were allowed to stand for 2 days in an atmosphere of 50% relative humidity.

TABLE I. Tensile Strength and Elasticity of Unplasticized Films from Guaran Triacetate, Cellulose Triacetate, and Potato Amylose Triacetate

Property	Guaran triacetate	Cellulose triacetate	Potato amylose triacetate
Tensile strength, kg./mm.^{2}	7.5	8.6	8.0
Elongation at break, %	4.0	4.0	17.0

Unplasticized films were prepared by the same techniques from cellulose triacetate (obtained from Tennessee Eastman Corporation) and potato amylose triacetate.

Stress-Strain Measurement. The dried strips of film (0.02-mm. thick and 10.00-mm. wide) were removed from the 50% relative humidity chamber, and their stress-strain characteristics were immediately determined on a Scott IP-4 inclined-plane serigraph (load capacity, 0-2000 g.). The distance between film clamps was set at 50 mm. for zero load. The tensile strength and elongation values are averages of at least ten tests conducted on at least two different films.

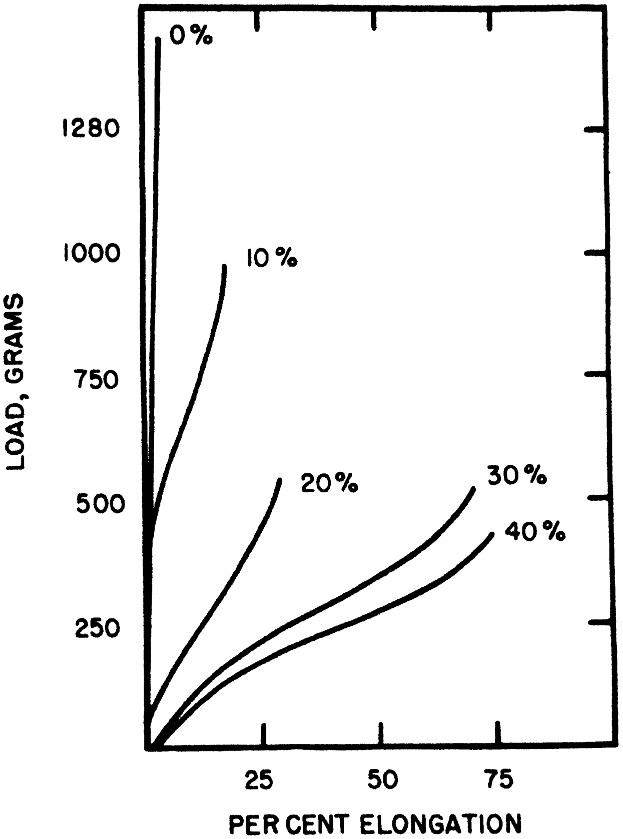

Fig. 2. Stress-strain curves of guaran triacetate (cross-sectional area 0.2 mm.^{2}) containing 0—40% dibutyl tartrate.

FILM CHARACTERISTICS

Guaran triacetate yields a colorless, transparent film whose tensile strength is sligthly lower than that for films from either cellulose triacetate or potato amylose triacetate, while its inherent plasticity corresponds to that of films from cellulose triacetate (Table I). The addition of plasticizer causes the film to become softer and more pliable (Fig. 2). As would be expected, a progressive weakening of the film occurs when increasing amounts of plasticizer are incorporated.

The unplasticized polymer is an almost ideal elastic material since Hooke's law is obeyed over most of the range. As stress is applied to plasticized guaran triacetate, indications of plastic flow are seen, and as elongation proceeds, evidences of increasing resistance to the applied stress are observed. The shattering of the elongated film in lines parallel to the direction of elongation is additional evidence of anisotropicity. These various properties are characteristic of linear molecules.

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Synopsis

Guaran triacetate, a linear molecule having one-unit branches, can be cast into clear, colorless films having a tensile strength of 7.5 kg./mm.^{2} and an elongation at break of 4%. Thus, it appears that one-unit branches of the size of the glycosidic unit do not adversely affect the film-forming properties of polysaccharide acetates. Plasticized films show more elasticity and greater elongation at break.

Résumé

Le triacétate de guarane, une molécule linéaire présentant des chainons latéraux unitaires, peut être coulé en films clairs et incolores, présentant une résistance à la tension de 7.5 kg./mm.^{2} et une élongation à la rupture de 4%. Il en ressort donc, que des chainons latéraux de la grandeur d'une unité glucosidique ne contrarient pas les propriétés de former des films chez les acétates des polysaccharides. Les fims plastifiés présentent une plus grande élasticité et une plus grande élongation à la rupture.

Zusammenfassung

Guarantriazetat ist ein lineares Molëkul, dessen Verzweigungsglieder aus einer Einheit bestehen. Es kann in einen klaren, farblosen Film von einer Zugfestigkeit von 7.5 kg./mm.^{2} und einer 4% igen Bruchdehnung gegossen werden. Dies deutet darauf hin, dass Verzweigungslieder, die aus einer Einheit von der Grösse der Glykosidgruppe bestehen, das Filmbildungsvermögen von Polysacchariden nicht ungünstig beeinflussen. Plastizierte Filme haben höhere Elastizität und grössere Bruchdehnung.

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LETTER TO THE EDITORS

NUMBER-AVERAGE MOLECULAR WEIGHT OF ACETALDEHYDE POLYMER

A sample of acetaldehyde polymer obtained from Professor M. Letort (1) was kept under vacuum in a refrigerator for about 48 hours to remove volatile decomposition products. Solutions of the polymer were made in methyl ethyl ketone and filtered. Osmotic pressure measurements were carried out at several polymer concentrations with a modified Fuoss-Mead osmometer in a constant temperature water bath at 27.7°C. The osmotic pressure π divided by the concentration c was plotted against concentration c and the graph extrapolated for the value π_0 at infinite dilution. The number-average molecular weight M_n was then calculated from the expression:

$$M_n = RT/\underset{c \rightarrow 0}{\pi_0}$$

where $R = 848$, $T = 300.7$, and $\underset{c \rightarrow 0}{\pi_0} = 0.5$ as per graph. A value of 5.1×10^5 was obtained for the sample of polyacetaldehyde under investigation.

The viscosity of the polymer in methyl ethyl ketone was determined with an Ostwald viscometer in a constant temperature water bath at 27.6°C. The specific viscosity divided by the concentration was plotted against concentration-giving a straight line. The intrinsic viscosity was obtained from the intercept-giving a value of 2.75 at 27.6°C.

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LETTER TO THE EDITORS

POLYPHENYL

The reaction between halogenated hydrocarbons and alkali or other metals leading to the union of two hydrocarbon radicals is well known and amply described in the literature as a Wurtz or Fittig reaction (1,2,3). Thus, diphenyl was first prepared by Fittig in 1862 by the reaction of monobromobenzene with sodium (2).

Similar partially successful attempts have been made by Busch and Weber (4) to link phenyl groups into chains by the reaction of disubstituted benzene derivatives, leading to chains with up to sixteen phenyl groups.

Previous attempts to condense dihalogen substituted benzenes with alkali to form "polyphenyls" have probably also been successful, but the products, not being "well-defined" in the classical sense, have not been described.

Preparation

A solution of p-dichlorobenzene in dioxane, toluene, or xylene was treated with about 2.4 gram-molecular weights of alkali metal per gram-atomic weight of the halogenated compound at the boiling point of the solution to yield close to 50% of the theoretical of a material with a molecular weight around 2700 soluble in nonpolar solvents. A typical preparation was as follows. One gram-molecular weight of commercial p-dichlorobenzene in 250 ml. of dioxane in a container equipped with a reflux condenser was treated with about 2.4 gram-atomic weights of sodium at the boiling point of the solution. Very little reaction occurred until boiling was violent enough to break up the chunks of molten sodium, when a violent reaction set in, which was controlled by appropriate cooling of the reaction vessel. Within about ten minutes the reaction slowed down to the point where no further visible change occurred. At this point the reaction mixture had a dark brown color and contained appreciable quantities of undissolved material. After 24 to 48 hours, virtually all the dioxane was distilled off, the excess sodium destroyed by a mixture of water and alcohol, and the reaction products separated. Refluxing the reaction products with water, followed by extraction in a Soxhlet extractor removed the inorganic products to the point where further extraction did not yield any chlorine-containing compounds in the water. Extraction with alcohol removed some material giving a light brown color to the extract.

Further extraction with benzene, toluene, or xylene yielded a dark brown solution, parts of which precipitated on the collecting flask but could be redissolved in an excess of the solvent. Part of the reaction products are insoluble in the nonpolar solvent. In this way, 30 to 35 g. of benzene, toluene, and xylene-soluble, methanol-insoluble material and an equal amount of product insoluble in benzene, toluene, xylene, methanol, carbon tetrachloride, and water was obtained from one gram-molecular weight of p-dichlorobenzene.

Properties

The product can be precipitated from solution by the addition of methanol. It can also be obtained by evaporating the solvent. In the first case it gave a tan fluffy powder, in the second a brown glassy material. On redissolving, the two products did not show any difference in properties. Cryoscopic molecular weight determinations in benzene containing 0.2 to 1.0 g. of product per 100 g. of benzene solution gave values of 2700 ± 100 to ± 500. The same value was obtained for samples prepared in different solvents, under a variety of concentration and temperature conditions. Similarly, material obtained as different fractions from a fractionation with methanol from benzene solution gave values within the same limits.

Chlorine analysis showed approximately six chlorine atoms per molecule. Hence the degree of polymerization is of approximately 34 six-membered carbon-rings units.* At 300^{o}C. the product did not melt or show any changes in properties or appearance. An ultraviolet spectrophotometer tracing showed an absorption maximum around 3000 A. indicating possible quinoid arrangement.** The specific viscosity divided by the concentration in grams per hundred mililiters of solvent in both benzene and xylene showed a marked decrease with increasing concentration, apparently leveling off at about 1 g. per 100 ml. (Fig. 1).***

A solution of the material temporarily inhibits the polymerization of styrene. On prolonged heating, polymerization of styrene takes place, however, without obvious decreases in brown color of the solution.

Discussion

It is tentatively assumed that the structure consists of six-membered carbon rings strung together essentially in the para position, showing marked quinoid arrangement.

The latter is supported by the position of the light absorption maximum (5) and by the influence of the material on polymerization.

It also is believed that the molecule is rigid and planar, the first from its relatively high viscosity and the second from the decrease of specific viscosity over concentration with concentration. If the molecule is planar and not too irregular, it can be assumed that two or

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*For this information the author is indebted to Mr. G. A. Edwards, University of Buffalo.

**For this information the author is indebted to Miss B. Levy, Polytechnic Institute of Brooklyn.

***For this information the author is indebted to Mr. T. Kane, Univversity of Buffalo.

more molecules may associate at higher concentration parallel to each other without materially influencing the length of the aggregates but decreasing their number.

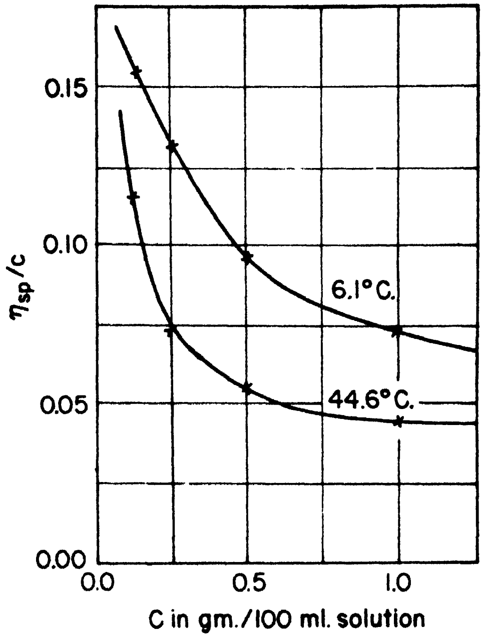

Fig. 1. Specific viscosity over concentration plotted against concentration of polyphenyl in benzene at 6.1°C. and 77.6°C.

The independence of the freezing point lowering and boiling point rise of concentrations between 0.5 to 1.0 g. per 100 g. of benzene cannot be fitted with the above explanation of the viscosity behavior.

It is as yet not possible to explain the position of the chlorine atoms in the molecule.

Conclusions

A polymer consisting probably of phenyl and quinoid groups linked in the para position, having a degree of polymerization of about 34 six-membered carbon rings, has been obtained.

Further work is being carried out on this polymer by varying the method of dehalogenation, the reaction temperature, and the concentration. Attempts are also under way to synthesize by this method other polymers, such as polyethylene, head-to-head, tail-to-tail polystyrene, and a carbon chain containing alternating single and double bonds. There are indications that it will thus be possible to obtain a series of new polymers.

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Errata: VISCOSITY FUNCTION FOR POLYELECTROLYTES

(J. Polymer Sci., 3, 603-604, 1948)

by Raymond M. Fuoss
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Page 604, column 1, 8-10 should read:

> poly-4-vinylpyridine. The molecular weights of the parent polymers for Salts I and II were 207,000 and 77,000.

Journal of Polymer Science Vol. IV, pp. 97-120, 1949

Polyelectrolytes. III. Viscosities of n-Butyl Bromide Addition Compounds of 4-Vinylpyridine-Styrene Copolymers in Nitromethane-Dioxane Mixtures*

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I. INTRODUCTION

In the previous paper of this series (1), some of the properties of poly-4-vinyl-N-n-butylpyridonium bromide were described. This compound is a long-chain strong electrolyte, prepared by the addition of butyl bromide to the polymer obtained from 4-vinylpyridine. In it, every other chain atom carries a ring in which the nitrogen atom is positively charged. The structure of the molecule in solution is presumably an open coil structure, differing from that characteristic of neutral chain polymers such as polystyrene in that the chain is more diffuse, due to repulsion between the positive pyridonium ions which are attached to the chain by primary valence bonds. The bromide ions are free-swimming kinetic entities, and may be roughly divided into two categories, depending on whether they are near (or "inside") a positive polyion or whether they are in the solvent between polymeric cluster ions. The fraction in the first category can be expected to decrease with dilution in a given solvent and to increase with decreasing dielectric constant at a given concentration if we assume that Coulomb forces between ions control their distribution. Now the intrinsic viscosity may be considered as a measure of the volume occupied by a polymeric structure in solution (2). A study of the viscosities of polyelectrolytes, therefore, might be expected to give information concerning the configuration of a given polyion in its dependence on the pertinent variables, concentration of electrolyte, and dielectric constant of solvent medium.

A further variable is available in the synthetic polyelectrolytes: the relative number of ionic groups within the chain. By making copolymers of vinylpyridine and a neutral monomer such as styrene, we obtain chains in which the number of ionogenic groups is proportional to the content of vinylpyridine. A determination of the copolymerization constants (3) gave $r_1 = 0.52$ and $r_2 = 0.62$ (with vinylpyridine as monomer 1 and styrene as monomer 2); therefore, copolymers of these two monomers, especially those prepared by only partial conversion, should have a uniform distribution of components in the chain, so that, for example, a 10% vinylpyridine copolymer would have as its average structure:

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**Results presented in this paper was abstracted from the thesis presented by George I. Cathers to the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1948.

$$(-S-S-S-S-S-S-S-S-S-P-)_n$$

where S denotes a styrene unit and P a vinylpyridine unit. By controlling polymerization conditions to get the same average* chain lengths for different copolymer ratios, we may then study the effect of charge density within the polymer coil at constant stoichiometric bromide ion concentration and constant permittivity of the solvent.

The purpose of this paper is to present (a) a description of the preparation of polyelectrolytes obtained by addition of n-butyl bromide to copolymers of 4-vinylpyridine and styrene, (b) a description of our viscometry technique, and (c) an account of the viscosities of these polyelectrolytes in solvents of different dielectric constant alone, and in the presence of other electrolytes. Our results show that the viscosities conform to the following empirical (4) equation:

$$\frac{\eta_{sp}}{C} = \frac{A}{1 + BC^{1/2}} + D \qquad (1)$$

where η_{sp} is the specific viscosity, C is concentration in grams solute per 100 cc. solution, and A, B and D are constants for a given system polyelectrolyte-solvent.

II. EXPERIMENTAL

Apparatus

Viscosities were measured in viscometers constructed according to Bingham's (5) design. Viscometer I had a capillary 11.0 cm. (1) long and 0.0148 cm. (r) radius and working volume 4.045 ml. (v). Using Bingham's equations (6), the constants C and C′ of the viscosity equation:

$$\eta = Cpt - C'\rho/t \qquad (2)$$

were calculated to be $C = 384.8\,r^4/vl = 4.15 \times 10^{-7}$ and $C' = 0.0446\ v/1 = 0.0164$. (in equation 2, η is viscosity, p is driving pressure in grams per square centimeter, ρ is density, and t is time in seconds.) The viscometer was in a thermostat held at 24.80° by means of an Aminco regulator. All solutions measured were pumped into the clean dry viscometer through a medium grade sintered glass filter.

Working pressures varied from about 30 to 200 cm. of water. The apparatus shown in Figure 1 was used to hold the driving pressure constant during a run; it depends on a slow steady overflow of water from an outlet set at the desired pressure level. The overflow outlet is set at a height above the water bottle A (to which it is connected with a piece of Tygon tubing) and air is pumped into the system by means of a bicycle pump, with the stopcocks to the viscometer closed. The water levels rise in the manometer (12 mm. I.D.) and in the Tygon tubing; when the water overflows at B, the stopcock to the pump is closed and a slow trickle of water into A is started. Bottle A has a cross section of about 200 $cm.^2$, so the 4-cc. volume change of the system during a viscosity determination only changes the pressure by 4/200 or 0.02 cm. The filter was packed with lamb's wool to keep dust out of the viscometer. Pressures were read on a steel scale hung beside the manometer and were corrected (7) to grams per square centimeter. The working volume of the manostat is fairly small, and pressure changes due to temperature changes were negligible. (The latter were especially annoying in a previous design, in which air was pumped into a carboy which in turn was connected to the viscometer and manometer; the adiabatic heat of compression caused pressure drifts which lasted for many minutes.)

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*Work on fractionated samples is in progress.

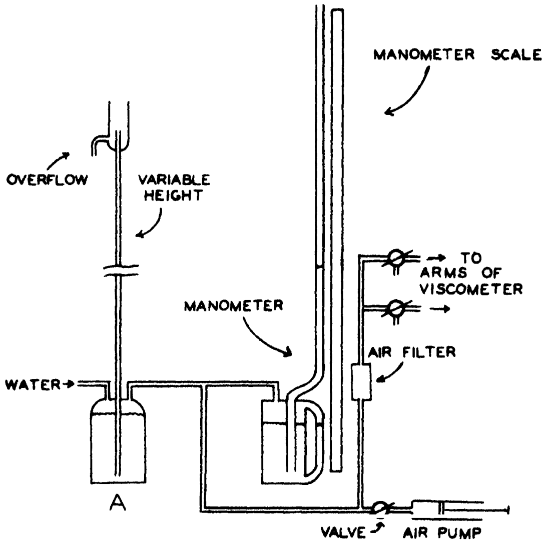

Fig. 1. Manostat for viscometer.

For calibration of the viscometer, a variety of liquids (see Table I) were used. Equation 2 may be written:

$$pt = \eta/C + C'\rho/Ct \tag{3}$$

and a plot of pt products against reciprocal time for liquids of known viscosity and density should therefore give the apparatus constants C and C′ via intercept and slope, respectively. In order to allow for the variable hydrostatic pressure head in the viscometer itself during a run, averages of flow times to right and to left for a given manometer setting were used; this hydrostatic head adds to the external driving pressure for flow in one direction and substracts from it for flow in the opposite direction. The pt - 1/t plots obtained were linear; the results are summarized in Table I. It will be seen that the average of the C values checks that calculated from the dimensions of the viscometer.

The calibration data showed, however, that equation 3 was inadequate to describe the behavior of our viscometer. While the pt - 1/t plots were indeed linear, the slope was not constant, as should be the case if kinetic energy (second term of equation 2) were the only correction needed. Incomplete drainage of the viscometer bulb would be a source of error if the drainage depended on the constants of the liquid under investigation. Barr (8) and Jones and Stauffer (9) have called attention to drainage errors. Swindells (10) avoided them by always running the test liquid into a dry viscometer; his procedure, however, is time consuming, and requires a battery of viscometers. We therefore determined the drainage error and made the appropriate correction. Let Δv be the volume retained on the walls of the viscometer bulb; we would expect it to depend on density ρ, viscosity η and time t as follows:

TABLE I. Viscometer Calibration at 24.80°.

Material	Intercept	Viscosity, cp.	$C \times 10^7$
Water	21556	0.8969[a,b]	4.161
"	-	0.8938[c]	4.146
20% sucrose	41400	1.715[d]	4.143
25% sucrose	51720	2.143[d]	4.143
30% sucrose	66685	2.769[d]	4.152

[a] J. F. Swindells, J. Colloid Sci., 2, 183 (1947).

[b] J. R. Coe and T. B. Godfrey, J. Applied Phys., 15, 625 (1944).

[c] "International Critical Tables," V, page 10.

[d] F. J. Bates et al., 'Polarimetry, Saccharimetry and the Sugars." Circular C440, National Bureau of Standards, Washington, D.C., 1942, page 673.

$$\Delta v = \beta v_0 \eta / \rho t$$

where β is a constant and v_0 is the volume of the dry bulb. Then, for emptying the bulb, the actual working volume v is:

$$v = v_0 - \beta v_0 \eta / \rho t$$

Since $C = k/v$, the viscometer equation then becomes to first-order approximation:

$$\rho t = \eta / C_0 + (C' \rho / C_0 - \beta \eta^2 / \rho C_0)/t = \eta / C_0 + \lambda / t \qquad (4)$$

where λ, the slope of the calibration curves, now includes corrections for both drainage and kinetic energy. The slope should satisfy the relation:

$$\lambda / \rho = C' / C_0 - (\beta / C_0)(\eta / \rho)^2 \qquad (5)$$

A test of equation 5 is shown in Figure 2 for data on the following systems: methyl ethyl ketone, water, 10% sucrose solution, 20% sucrose, 91.4% ethanol, 25% sucrose, 30% sucrose and 45.7% ethanol. The vertical lines in Figure 2 mark the extreme values of the slopes consistent with the data; the sequence of points from left to right is the sequence of solutions as enumerated above. Except for the 30% sucrose solution and the two ethanol-water mixtures, the data satisfy equation 5. From the intercept at $(\eta/\rho) = 0$, which equals C'/C_0, we calculate $C' = 0.0172$, which is in fair agreement with the value calculated for the coefficient of the kinetic energy correction from the dimensions of the viscometer.

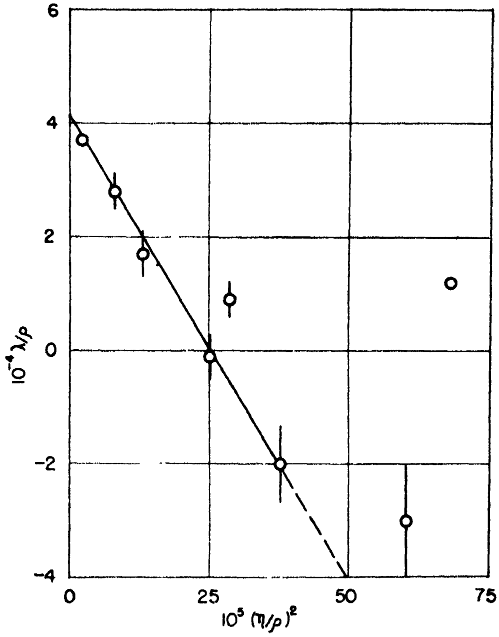

Fig. 2. Test of equation 5.

For practical work, equation 5 was used in the approximately equivalent form:

$$\begin{aligned}\lambda/\rho &= C'/C_0 - \beta C_0 (pt/\rho)^2 \\ &= 4.15 \times 10^4 - 2.77 \times 10^{-5} (pt/\rho)^2 \qquad (5a)\end{aligned}$$

It would, of course, be misleading to determine the viscosities of the polymer solutions by measuring at a series of pressures and extrapolating the pt - 1/t curves to infinite time (zero rate of shear) because the viscosities of such solutions in general depend on the rate of shear. Consequently, equation 5a was used to correct the observed pt products, and viscosities were calculated as:

$$\eta = [(pt)_{obs.} - \lambda_{calc.}/t_{obs.}]C \qquad (6)$$

Any remaining dependence of viscosity on driving pressure was assumed to be that inherent in the structure of the solute. It should also be mentioned that, with our viscometer and pressure range, the correction of equation 5a is negligible for viscosities greater than about 2 centipoises, because the time then becomes large.

A second viscometer (II) was also used: its constants were $C = 1.091 \times 10^{-6}$, $C' = 0.01615$, and λ/ρ $1.480 \times 10^4 - 2.73 \times 10^{-5} (pt/\rho)^2$

Materials

Copolymers and Salts

The monomers, 4-vinylpyridine (Reilly Tar and Chemical Corporation), and styrene (Dow N-99), were redistilled under vacuum shortly before use, in order to separate them from inhibitor and oxygen. Copolymerizations were carried out in 20% toluene solution at 80° with 1% of benzoyl peroxide as catalyst; the toluene had previously been boiled to expel oxygen and the reaction vessel was swept out with nitrogen. Presence of oxygen invariably gave reddish products. The polymerizations were usually interrupted after about 30% conversion or less, so that the composition of the products would be reasonably uniform. The copolymers were then precipitated. Since styrene is nonpolar and pyridine is quite polar, each different copolymer required a different treatment, because polar liquids are obviously solvents for the pyridine-rich copolymers and precipitants for the styrene-rich compounds, while the reverse is true for nonpolar liquids. It therefore is necessary to describe the procedure for each copolymer separately.

Analyses of the purified copolymers for nitrogen were made by the semimicro-modification (11) of the Dumas combustion method. (Kjeldahl (12) analyses were hopelessly erratic.) It was necessary to match the amount of reprecipitated polystyrene used as blanks rather closely to the amount of copolymer sample used, because the size obviously must increase as the vinylpyridine content decreases, and the magnitude of the blank correction depended on the size of hydrocarbon sample burned. Unless care is taken, the combustions tend to go too rapidly towards the end; we found it necessary to take as much as three hours for a 150-mg. sample.

Given the nitrogen content expressed as the fraction f of nitrogen by weight, the mole fraction F of vinylpyridine in the copolymer may be calculated. If we have m moles of vinylpyridine and n moles of styrene, then by definition:

$$F = m/(m + n)$$

Since:

$$f = mN/(mP + nS) \qquad (7)$$

where N, P, and S stand for the corresponding molecular weights, we have:

$$F = fS/(N - Pf + Sf) \qquad (8)$$

which simplifies to:

$$F = Sf/(N - f) \qquad (8a)$$

since styrene and vinylpyridine differ by unity in molecular weights. By differentiation, we find the error ΔF in F due to an (absolute) error Δf in f to be:

$$\Delta F = 1120\Delta f/(14 - f)^2$$

or approximately:

$$\Delta F = 5.7\Delta f \qquad (9)$$

because f can never exceed 0.133, the fraction of nitrogen in vinylpyridine.

Salts were prepared from the copolymers by addition of n-butyl bromide (Eastman), which was washed with 5% sodium carbonate solution and water, treated with Drierite, and distilled. The addition of alkyl halides to amine nitrogen (13,14) is favored by the presence of polar solvents. Butyl bromide is itself a good solvent for copolymers containing up to about 40% vinylpyridine, but the corresponding salts are insoluble. Conversion of the polar pyridine nitrogen to an electrolytic pyridonium nitrogen enhances the problem of solvent medium, because the styrene part of the molecule is insoluble in liquids which are good solvents for electrolytes. After some preliminary experiments, nitromethane was chosen as solvent to be used in increasing amounts as the fraction of vinylpyridine in the copolymer increased. Some side reaction, involving the aci — form of nitromethane was expected; in order to avoid pyridonium salts of $CH_2{=}NO_2$ in the product, an excess of butyl bromide over pyridine content was always used, so that the irreversible quaternization reaction would prevail. For the samples with high styrene content, it was found necessary to add some dioxane to keep the system homogeneous. Again, each composition presented a special problem, and details of the syntheses will be given for each compound.

Some of the salts were analyzed for bromine by the Parr semimicro-bomb method (15). However, the method was inconvenient for the styrene-rich copolymers because the sample became awkwardly large. Furthermore, we preferred to use a method which would analyze for only bromide ion, rather than total bromine, to make certain that no side reactions had occurred. Conductimetric titration in 50-50 dioxane-water solution of a 5% vinylpyridine copolymer with aqueous silver nitrate gave fair results, but equilibrium was slow in establishing itself. (This time lag was possibly a measure of the rate of exchange of bromide ions within the chain electrolyte with nitrate ions in the solution.) A simplified potentiometric method was then devised. As electrodes, a silver wire and a Beckman glass electrode were used, and voltages were read on a Beckman pH meter. The sample was dissolved in 50-50 water-acetone (redistilled), to which a few drops of concentrated nitric acid were added (to keep the potential from swinging through zero.) The solution was stirred constantly during the addition of aqueous silver nitrate; equilibrium was attained quite rapidly, and very sharp breaks of about 150 mv. characterized the end-point. The method was checked by titrating potassium bromide test samples. One sample of copolymer salt (No. 6.6) was analyzed by both methods with the following results: Parr, 4.66, 4.71% Br; potentiometric, 4.79, 4.81% Br.

Given the weight fraction of bromine f' in the salt,

$$f' = m\,\mathrm{Br}/(nS + mP + m\,\mathrm{BuBr})$$

the mole fraction F of vinylpyridine in the copolymer salt is:

$$\begin{aligned} F &= Sf'/[\mathrm{Br} - (\mathrm{BuBr} + P - S)f'] \\ &= 104.15\,f'/(79.92 - 137.02\,f') \end{aligned} \tag{10}$$

and the error ΔF corresponding to an absolute error $\Delta F'$ in bromide content is found to be:

$$\Delta F = 8320\,\Delta f'/(80 - 138\,f')^2 \tag{11}$$

a quantity which can vary from zero to 7.0 times $\Delta f'$. According to equations 9 and 11, we see that the calculated copolymer composition is quite sensitive to both nitrogen and bromide content.

We now proceed to a detailed description of the different copolymers and salts: for convenience in reference, the following table gives our sample numbers and mole fractions of vinylpyridine calculated from bromide content in the compounds used. In this paper, the code numbers of the second column will be used; they are the rounded mole percentages of vinylpyridine in salts.

TABLE II. Composition of Copolymer Salts.

Sample	Code	Br, %	Method	F
C51	1.5	1.145	Ptm.	0.0152
B94	6.3	4.49	Parr	0.0632
B134	6.6	4.68	Parr	0.0664
D41	13	8.48	Ptm.	0.130
B132	26	14.69	Parr	0.256
C125B	58	25.25	Ptm.	0.583
C125C	78	29.40	Ptm.	0.778
C132	90	31.6	Ptm.	0.898

Salt No. 1.5. A mixture of styrene and vinylpyridine containing 0.99 mole per cent of the latter was heated for 8 hours at 80° in 20% toluene solution. The polymer was precipitated as a gum by pouring the solution into 2 volumes of methanol. The gum was dissolved to give a 17% solution in methyl ethyl ketone which was precipitated in 5 volumes of methanol. The resulting granular precipitate was redissolved in methyl ethyl ketone (5% solution) and reprecipitated in 5 volumes of methanol; yield, 29.5%. 30 g. of vacuum-dried copolymer was then heated for 22 hours at 80° under a nitrogen atmosphere in a mixture consisting of 140 g. nitromethane, 160 g. dioxane, and 6.7 g. butyl bromide. The solvent was then removed under low pressure at 60° and the residue taken up in methyl ethyl ketone to give a 30% solution. A gum was obtained when this solution was poured into 5 volumes of methanol. The gum was made up to 5% solution in benzene; a dry, porous powder was finally obtained by subliming the benzene as recommended by Lewis and Mayo (16). The product is soluble in ketones, dioxane and benzene, swells in nitrobenzene and alcohol, and is insoluble in petroleum ether and water.

Salts No. 6.3 and 6.6. The feed was 4.72 mole per cent vinylpyridine. Samples were taken at 8.5, 9.5, and 21.5 hours, with conversions 27.0, 30.9, and 34.3%. Ethanol was found to be the best precipitant for the 5% vinylpyridine range. Accordingly, the 20% toluene reaction mixture was poured into 5 volumes of ethanol; the resulting precipitate was redissolved to 5-10% solution in methyl ethyl ketone and reprecipitated in 5 volumes of ethanol. Salts were made by heating for at least 20 hours at 80° in 10% solution in a 3:1 mixture of nitromethane and butyl bromide. The solvent was then evaporated under vacuum, and the residue made up to 10% solution in acetone. On pouring into 4 volumes of petroleum ether, a gum was obtained which was dissolved in benzene. On subliming the benzene, a fine, porous powder was obtained. Two samples of salt No. 6.3 were analyzed for bromine by the Parr method; found, 4.55 and 4.43% Br, average 4.49%. The Dumas nitrogens on two samples of the parent polymer were 0.856, 0.857%, from which the calculated bromide content of the salt was 4.50%, in excellent agreement with the value found in the Parr analyses. The salt is soluble in nitromethane, ketones, and dioxane, disperses in benzene, and insoluble in petroleum ether, tert-butanol, and water.

Salt No. 13. The feed was 9.95 mole per cent vinylpyridine, heating time 6 hours, conversion 29.4%. The reaction mixture was precipitated in 5 volumes of petroleum ether; the resulting gum was made up to 10% in toluene and reprecipitated in 5 volumes of petroleum ether. The gummy precipitate was then made up to 10% solution in methyl ethyl ketone and precipitated in 10 volumes of petroleum ether. The last step was repeated once. To prepare the salt, 4.5 g. copolymer, 10 ml. butyl bromide, and 50 ml. nitromethane were heated for two days at 80°, after which the solvent was removed by evaporation under vacuum. This sample was used without further purification.

Salt No. 26. The feed was 19.86 mole per cent vinylpyridine, heating time 5 hours, conversion 18.4%. A yellow gum was obtained by precipitation of the toluene reaction mixture in 1.5 volumes of petroleum ether; made up to 10% solution in methyl ethyl ketone and precipitated in 10 volumes of petroleum ether, a white gum was obtained. On sublimation, a 5% solution in benzene left a porous powder. The product was made up to 4.2% solution in a 95:5 mixture of nitromethane and butyl bromide. After heating for 41 hours at 80°, the reaction mixture was poured into 3 volumes of dioxane. The oil which separated was made up to 15% solution in nitromethane, and, on pouring into 12 volumes of dioxane, a heavy resin separated. The resin was dispersed in water; addition of dioxane gave a clear solution, although the resin is not soluble in dioxane alone. The solution was evaporated, and the residue dried to a constant weight in vacuum at 40°. It is insoluble in petroleum ether, benzene, and ketones. Parr analyses gave 14.76 and 14.62% Br, average 14.69%. From this, we calculate 3.22% nitrogen in the parent polymer, which compares favorably with 3.18% found.

Salt No. 58. The feed was 59.8% vinylpyridine; after 1.3 hours, polymer started to precipitate and the reaction was terminated by pouring into 3 volumes of petroleum ether. The resulting gum was made up to 5% solution in methyl ethyl ketone and reprecipitated in petroleum ether. No combination of solvent-precipitant could be found which would give a granular precipitate. With the vinylpyridine content so high, the polymer is no longer soluble in benzene. We found tert-butanol (m.p. 25.4°, b.p. 82.8°) to be a good solvent for the polymer, however, and its constants are such that the Lewis-Mayo (16) technique works very well. A 4% solution of the copolymer tert-butanol left a porous powder on sublimation of the frozen solvent. Salt was prepared by heating a 3% solution of the polymer in 80-20 nitromethane-butyl bromide for 112 hours at 50°. The reaction mixture was precipitated as an oil by pouring into 10 volumes of dioxane. The oil was diluted to 2.5% in ethanol, and a precipitate was obtained on pouring into 20 volumes of dioxane. As usual, the salt was dried to constant weight in vacuum. Salts containing more than about 20% vinylpyridine are hygroscopic and must be kept in desiccators. This salt in soluble in alcohols and water.

Salt No. 78. The feed was 79.8 mole per cent vinylpyridine; after 50 minutes, solid started to precipitate and the reaction was terminated by pouring the mixture into three volumes of petroleum ether. The yield for this polymer (and the previous one) was only about 6-7%; the low conversion was, of course, due to the quenching. The gum was made up to 7% solution in tert-butanol and recovered as a porous powder by lyophile drying. Salt was prepared by heating for 112 hours at 50° in 2.5% solution in an 80–20 nitromethane–butyl bromide mixture. The product was precipitated in 10 volumes of dioxane and reprecipitated from 2.5% ethanol solution in 10 volumes of dioxane. The properties are similar to those of No. 58.

Salt No. 91. This salt was prepared from the polyvinyl pyridine described by Fuoss and Strauss (1), by heating a 4% solution in 80–20 nitromethane–butyl bromide for 112 hours at 50°. Purification was as previously described. Dumas nitrogen on the salt was 5.52%, vs. 5.79% theoretical, i.e., 95.3% of theoretical. Potentiometric bromide on the salt was 31.3, 31.6, 31.8%, average 31.6%, vs. 33.02% theoretical, i.e., 95.2% theoretical. Hence there is one bromide ion for each nitrogen atom in the polysalt. If we calculate F, the mole fraction of vinylpyridine from the observed bromide content by equation 10, we obtain 0.898. The apparent contradiction (cf. equation 11) between 95.3% and 89.8% "purity" lies, of course, in the fact that the former figure refers to composition by weight and the latter to mole fraction. In order to be self-consistent, we shall calculate polyelectrolyte concentrations as actual grams of ("impure") salt per 100 ml. solution (C) or as stoichiometric equivalents (c) of bromide per liter, the latter figure being based on the bromide analysis. When we compare different copolymers, we shall use the mole fraction scale F, based on equation 10 and the bromide analyses, despite the fact that this puts the salt of polyvinyl pyridine at 0.9 instead of at 1.0 on the 0-1.0 styrene-vinylpyridine scale.

Cross-Linked Copolymers. By adding ethylene dibromide to our copolymers in nitromethane solution, we obtained cross-linked gels which were completely insoluble in all solvents tested. The nitromethane could be removed under vacuum, leaving the resin as a brittle porous solid. These resins are, of course, insoluble, because pyridine nitrogens in different chains are linked by dimethylene groups. We thus have a strong electrolyte as an insoluble resin, with anchored cations and diffusible anions. Further investigation of these anion exchange resins is in progress.*

*The compounds described above are specific examples of a general class of anion exchange resins, in which a polymer containing tertiary nitrogen groups is cross-linked by the addition of dihalides. A

The above description shows that the properties of the copolymers and their salts gradually shift as we go from styrene-rich to pyridine-rich compounds. Toluene and other aromatics are good solvents for the polymers up to about 50% vinylpyridine, methyl ethyl ketone up to about 80%. Dioxane and butyl bromide are solvents up to 40%. Nitromethane is a good solvent in the intermediate range 20-50%; addition of butyl bromide increases the solvent power. Methanol or ethanol precipitate polymers with less than 5% vinylpyridine; the intermediate range swells in alcohols; and the pyridine-rich polymers are soluble. None are soluble in petroleum ether. The salts start by being soluble in dioxane and insoluble in water and nitromethane. As the content of vinylpyridine increases, these roles are reversed.

Solvents

Dioxane. Eimer and Amend dioxane was refluxed over sodium hydroxide and distilled. Final drying was over sodium, from which it was distilled through a 1 x 18-in. Stedman column. The middle fraction, boiling at 100.8-100.9° was used. Its conductance was about 10^{-14} mho.

Nitromethane. Eimer and Amend nitromethane was dried over phosphorus pentoxide and distilled through the Stedman column. B.p. 100.8 - 100.9°. The conductance was $1\text{-}5 \times 10^{-7}$ mho immediately after distillation; it increased slowly on standing, perhaps due to shift of nitromethane to the aci-form, which is ionogenic. The viscosity also varied slightly with time; extreme values were 0.6208-0.6236 cp. The viscosity of this solvent was accordingly checked before or after each run in order to avoid spurious values of relative viscosity.

Solvent densities were measured at 25°. The following values were found: dioxane, 1.027; 60.0 dioxane - 40.0 nitromethane, 1.064; 40.0-60.0, 1.084; 17.0-83.0, 1.103; nitromethane, 1.124.

Dielectric constants of a series of dioxane-nitromethane mixtures were also determined, using the Shedlovsky bridge (17) as a substitution bridge with a calibrated air condenser parallel to the cell. Corrections for lead capacity were made by measuring the capacity of the system with several liquids of known dielectric constant (air, toluene, acetone, and nitromethane) in the cell. The results are summarized in Table III.

III. RESULTS

Copolymerization Constants

From our data on conversion and nitrogen content of the copolymers, it was possible to calculate the copolymerization constants (3) r_1 and r_2, using the method of Lewis and Mayo (18). In Table IV are given in successive columns the mole per cent vinylpyridine in the feed, the percentage conversion at the time the samples were taken, the percentage of nitrogen in the copolymer obtained, the mole per

patent letter describing these resins has been sent to the legal department of the Office of Naval Research.

TABLE III. Dielectric Constants of Nitromethane-Dioxane Mixtures.

CH_3NO_2, wt. %	ε'	CH_3NO_2, wt. %	ε'
0.0	2.2	73.5	28.4
38.8	15.6	82.0	31.9
52.2	20.3	89.9	35.0
64.1	24.7	100.0	39.4

cent of vinylpyridine in the copolymer, the values of the arbitrary parameter p, and the corresponding values of r_1 and r_2 calculated by means of equations 12 and 13 of the reference just cited. The corresponding test plot is given in Figure 3; from the intersections, we find:

$$r_1 = 0.52 \pm 0.06$$

$$r_2 = 0.62 \pm 0.02$$

which means that each monomer has a higher probability of adding to the free radical derived from the other monomer.

TABLE IV. Calculation of Copolymerization Constants.

Feed	Yield	N, %	F	p	r_1	r_2
4.72	27.0	0.8905	6.62	0.1	0.963	0.628
				2.0	0.210	0.605
4.72	34.3	0.8566	6.37	0.5	0.819	0.638
				2.0	0.242	0.621
19.83	26.5	3.18	23.7	0.5	0.843	0.686
				2.0	0.120	0.560
39.8	27.4	5.49	40.9	0.5	0.927	0.855
				1.2	0.545	0.621

Osmotic Pressures

We are indebted to Dr. Wilhelm Albrink of the Yale Medical School for measurements of the osmotic pressures (19) of two copolymers and of a sample of polystyrene in methyl ethyl ketone at 25°. All three polymers were obtained by solvent polymerization at 80° in 20% toluene solution at conversions of about 30%. Polymer 5E contained 6.37% vinylpyridine and 6D 40.9%, as calculated from Dumas nitrogens of 0.857% and 5.49%. The data are given in Table V together with the molecular weights M_n calculated from the intercepts at $\pi = 0$ on $\pi/w - w$ plots. Here π is osmotic pressure in centimeters of solvent and w is concentration in grams solute per kilo solution. We recall that polyvinylpyridine prepared under similar conditions (1) had a number-average molecular weight of 77,000. For our present purposes, it seems safe to assume that the molecular weights of the copolymers used in this research were in the range 50–80,000.

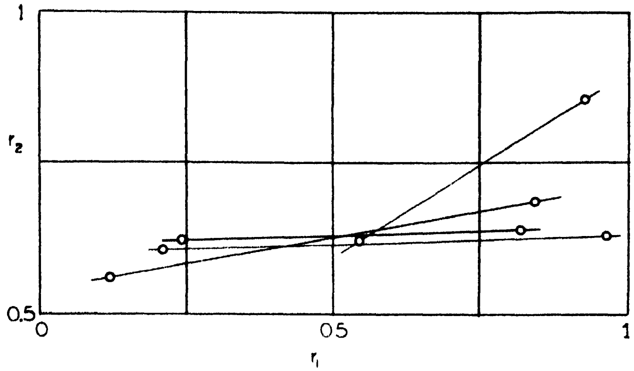

Fig. 3. Determination of copolymerization constants.

Viscosities of Copolymers

In order to obtain a comparison between the different copolymers, viscosities were determined in methyl ethyl ketone at 24.8°. A sample of the polystyrene used for osmotic pressure determination was also measured in methyl ethyl ketone and in toluene. The intrin-

TABLE V. Osmotic Pressures and Molecular Weights.

w	π	π/w
Polystrene, M_n = 50,000		
10.16	4.94	0.495
5.75	2.82	0.503
3.07	1.54	0.500
0.00	---	(0.500)
Copolymer 5E, M_n = 80,000		
8.49	3.36	0.394
6.23	2.35	0.376
3.33	1.16	0.348
0.00	---	(0.317)
Copolymer 6D, M_n = 72,000		
9.31	3.28	0.35
5.19	1.66	0.32
3.09	1.20	0.38
2.94	1.09	0.37
0.00	---	(0.35)

sic viscosities are all low and of the same order of magnitude, indicating that the molecular weights are all in the same range. There is, perhaps, a slight upward trend with increasing vinylpyridine content. These results are summarized in Table VI.

TABLE VI. Intrinsic Viscosities of Copolymers in Methyl Ethyl Ketone.

ViPy, %	[η]	ViPy, %	[η]	ViPy, %	[η]
0.	0.128	5.	0.139	20'.	0.172
0*	0.163	10.	0.141	30	0.145
1.	0.131	20.	0.160	40	0.153

*Polystyrene in toluene

Viscosities of Polyelectrolytes

The experimental results for a variety of systems are summarized in Tables VII—XII, in which concentrations C (grams solute per 100 ml. solutions) and reduced viscosities $z = \eta_{sp}/C$ are given.

TABLE VII. Viscosities of Polysalts in Methyl Ethyl Ketone.

C	η_{sp}/C
Salt No. 1.5	
0.264	0.1633 ± 0.0039
0.564	0.1601 ± 0.0019
1.279	0.1638 ± 0.0009
1.835	0.1693 ± 0.0007
2.46	0.1789 ± 0.0006
3.30	0.1890 ± 0.0005
Salt No. 6.6	
0.497	0.1472 ± 0.0022
0.920	0.1382 ± 0.0012
2.20	0.1588 ± 0.0006
2.85	0.1673 ± 0.0005

For the systems reported here, no dependence of viscosity on rate of shear was found within the limit of experimental error.

TABLE VIII. Viscosities of Polysalts in Nitromethane.

C	η_{sp}/C	C	η_{sp}/C	C	η_{sp}/C
Salt No. 6.6		Salt No. 26		Salt No. 90	
0.0339	0.599	0.0122	3.52	0.00122	6.05
0.1399	0.380	0.0421	2.06	0.00602	3.85
0.613	0.241	0.1511	1.210	0.01760	2.54
2.39	0.182	0.702	0.686	0.0252	2.22
		3.135	0.454	0.1185	1.276
				0.1963	1.043
Salt No. 13		Salt No. 58		0.579	0.704
0.0902	0.890	0.00365	4.76		
0.1925	0.681	0.01827	2.72		
0.435	0.510	0.0784	1.453		
0.909	0.400	0.337	0.807		
2.15	0.312	1.594	0.470		

IV. DISCUSSION

In methyl ethyl ketone (Table VII), Salts 1.5 and 6.6 give reduced viscosities which are of the same order of magnitude as those of the parent polymer. There is, however, a significant difference in the shapes of the curves: while the z - C curves for all the neutral poly-

TABLE IX. Viscosities of Salt No. 26 in Solvent Mixtures.

I. 83.0 CH_3NO_2 - 17.0 $C_4H_8O_2$, $\eta_0 = 0.006591$
II. 60.0 CH_3NO_2 - 40.0 $C_4H_8O_2$, $\eta_0 = 0.007292$

I		II	
C	η_{sp}/C	C	η_{sp}/C
0.0561	1.279	0.1029	0.545
0.1298	0.925	0.1858	0.444
0.248	0.744	0.357	0.356
0.465	0.600	0.682	0.302
1.012	0.468	1.572	0.252
2.090	0.389		

TABLE X. Viscosities of Salt No. 90 in Solutions of Tetrabutylammonium Bromide in Nitromethane.

I. 10^{-3} N Bu_4N Br, η_0 = 0.006249
II. 10^{-2} N Bu_4N Br, η_0 = 0.006289
III. 10^{-1} N Bu_4N Br, η_0 = 0.006742

I		II	
C	η_{sp}/C	C	η_{sp}/C
0.0243	0.510	0.0281	0.204
0.0594	0.565	0.1063	0.262
0.0961	0.588	0.310	0.278
0.1160	0.597	0.834	0.288
0.242	0.580	2.160	0.298
0.342	0.573	III	
0.469	0.556	0.1462	0.1395
0.636	0.530	0.275	0.1536
1.099	0.484	0.475	0.1581
1.907	0.429	0.940	0.1625

mers in this solvent are of the familiar linear type, the curves for the salts show a shallow minimum below about 1% concentration. As we go to solvents of higher dielectric constant, this tendency of the reduced viscosity to increase with dilution becomes more marked, and with nitromethane ($\varepsilon' = 39.4$), the reduced viscosity of the polyelectrolyte is better than an order of magnitude larger than the intrinsic viscosity of the parent polymer. This behavior seems to be general for strong electrolytes of high molecular weight: Heidelberger (20) found it for the sodium salt of Type III pneumococcus polysaccharide in water, Staudinger (21) for sodium polyacrylate in water, and we have observed it for a number of systems, aqueous and non-aqueous.

The viscosity rises so rapidly with dilution that the conventional z - C scale is useless for a presentation of the data. Since long range electrostatic forces are obviously involved, it seemed logical to look for a square root term in the viscosity function; our first approximation (1) suggested a linear dependence of $\eta_{sp}/\sqrt{C}$ on $\sqrt{C}$, but further investigations in more dilute solutions showed that this function was too simple. Based on the data of Tables VIII and IX, we find that the following equation reproduces the experimental results for all of the polyelectrolytic systems which have been studied:

$$z = \frac{\eta_{sp}}{C} = \frac{A}{1 + BC^{1/2}} + D \qquad (12)$$

Here A, B, and D are empirical constants. When D is negligibly small compared to z, a plot of 1/z is linear in the square root of concentration and A and B may be determined from the slope and intercept.

TABLE XI. Viscosities of Salt No. 26 in Solutions of Tetrabutylammonium Bromide in Nitromethane.

I. 10^{-3} N Bu_4N Br, $\eta_0 = 0.006239$

II. 10^{-2} N Bu_4N Br, $\eta_0 = 0.006289$

III. 10^{-1} N Bu_4N Br, $\eta_0 = 0.006742$

I		II	
C	η_{sp}/C	C	η_{sp}/C
0.0489	0.605	0.0420	0.231
0.0888	0.678	0.1629	0.315
0.1261	0.681	0.444	0.351
0.1341	0.688	1.207	0.367
0.1761	0.685	3.005	0.374
0.2145	0.685	III	
0.250	0.684	0.140	0.192
0.323	0.665	0.261	0.194
0.392	0.657	0.437	0.200
0.545	0.621	0.795	0.205
1.080	0.545		
1.151	0.536		
3.41	0.436		

When D is not negligible, it can be determined to first approximation as the intercept at C = ∞ on a plot of z against $C^{-1/2}$ as shown in Figure 4 for Salt 26 in three different solvents. Having determined D, several methods of obtaining A and B are possible. A plot of 1/(z - D) = 1/z′ is linear in $\sqrt{C}$, as is shown in Figure 5 for the systems treated in Figure 4. This method gives a very good value of B/A as the slope, but when A is large, the intercept 1/A is almost invisible. Furthermore, the plot is not very sensitive to D. Its advantage is that most weight is given to points in the range of higher concentrations where the precision is better. A second method is to calculate:

$$y = (z - D)C^{1/2} \tag{13}$$

and plot 1/y against 1/ $\sqrt{C}$ as is shown in Figure 6 for Salt 26 in the 83% nitromethane - 17% dioxane mixture. The three curves shown correspond to D = 0.15, 0.18, and 0.20. It will be noted that the plot

for D = 0.18 is approximately linear, while that for D = 0.20 runs concave-upward and for D = 0.15 concave-downward. This plot is much more sensitive than the first one described, and permits determination of both A and B as well as D. It magnifies experimental errors and heavily weights the data at low concentrations in determining A from the slope. Here a good value of B/A (as intercept) is again obtained, and since the curvature is so sensitive to D, a reliable value of this constant can also be found.

The constants for the systems of Tables VIII and IX are given in Table XIII. It will be noted that the values of D are uniformly small and about the same size as the intrinsic viscosities of the parent polymers. Unfortunately the data for Salt 26 in two solvents scattered so badly that only D and the ratio B/A could be determined. If we disregard this gap in the series, we see a trend of A toward larger values as the fraction of vinylpyridine increases. This seems reasonable if we recall that at zero concentration, z approaches $z_0 = (A+D)$, and z_0 the limiting reduced viscosity is the analog of $[\eta]$, the intrinsic viscosity of ordinary polymers. Since $D \ll A$, $z_0 \approx A$, and if we assume that A is a measure of the polymer coil at infinite dilution, we would expect A to increase with vinylpyridine content in the copolymer because intramolecular Coulomb repulsion between like charges must necessarily increase as the pyridonium content rises, and the chain will open up more the higher the charge concentration.

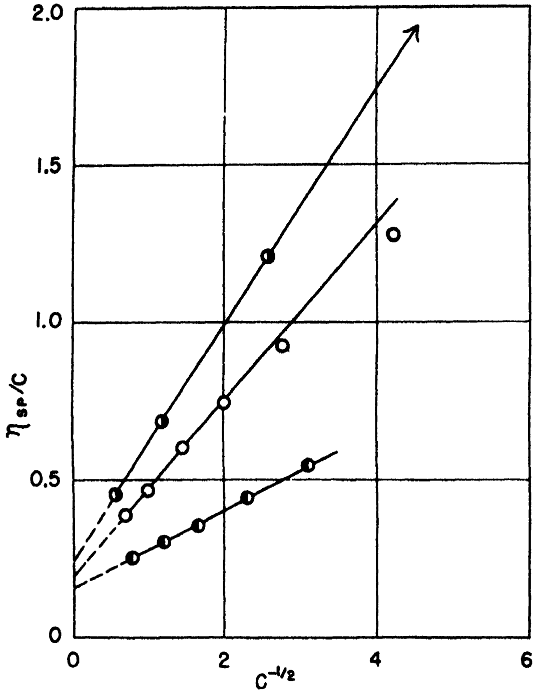

Fig. 4. Determination of constant D for Salt 26 in 60-40 (◐), and 83-17 (O) nitromethane-dioxane mixtures and in nitromethane (◐).

If we assume that A is the same for Salt 26 in the three solvents studied (with dielectric constants 39.4, 32.1, and 23.1), then the change of B/A measures the change of the electrostatic term $B\sqrt{C}$ with changing solvent. It will be seen that B/A increases as the dielectric constant of the solvent decreases; empirically, not quite as fast as $(1/\varepsilon')^2$. This result also seems reasonable because electrostatic interaction increases in intensity as the dielectric constant of the medium decreases. Given these clues to the possible physical significance of the terms in equation 11, we can now plan a more systematic attack on the problem than the present exploratory survey.

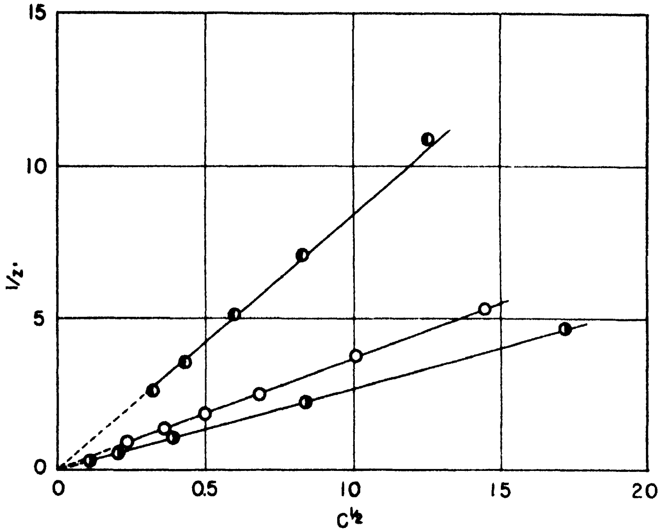

Fig. 5. Test of equation 11 (same code as Figure 4).

If the viscosity data for the different copolymers are plotted on any scale, it will be observed that there is not much difference between the curves for Nos. 90, 58, and 26 in the finite range of concentrations. This is perhaps best substantiated by the fact that B/A for these three salts has the values 2.42, 2.48, and 2.60, respectively. Salt 90 has an ionic group in (nearly) every monomer unit, Salt 58 has three out of five, and Salt 26 one of four. This must mean that the configuration of these three salts in solution must be not greatly different, des-

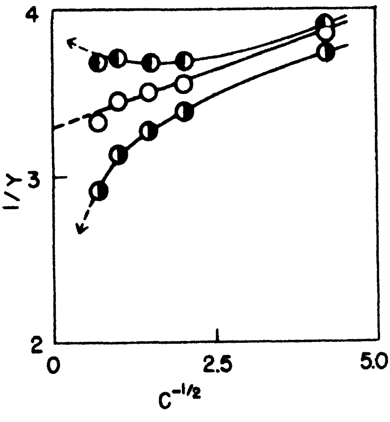

Fig. 6. Test of equation 12.

pite the large difference in the relative number of ionic centers. If no association occurred, we would expect Salt 90 to have the most extended configuration, and this is probably true at infinite dilution. But at finite concentrations the pyridonium ions in the chain hold bromide ions in their vicinity by Coulomb attraction and the positive ions in these associated ion pairs cannot contribute to an expansion of the coil by mutual repulsion; as a matter of fact, the pairs act as dipoles and may well compress the coil by dipole-dipole attraction. Consequently, in the range of high vinylpyridine content, we have two competing influences: potentially, the pyridonium groups could repel each other and open the coil, while actually their high charge density draws negative counter ions into the coil and permits it to contract. It is only when the relative spacing of pyridine groups along the copolymer chain becomes large enough to weaken electrostatic interaction that a change of viscosity with copolymer ratio becomes apparent; at 13% vinylpyridine, B/A is 3.88 and at 6.6% has risen to 8.85. The limit B/A = ∞ corresponds, of course, to an uncharged polymer, for which, in our notation, z = D.

TABLE XII. Viscosities of Polysalts in 10^{-3} N Solutions of Tetrabutylammonium Bromide in Nitromethane.

I, Salt No. 6.6
II, Salt No. 58; $\eta_0 = 0.006241$

I		II	
C	η_{sp}/C	C	η_{sp}/C
0.1644	0.1690	0.0761	0.512
0.235	0.1830	0.1511	0.554
0.334	0.1888	0.255	0.560
0.465	0.1880	0.440	0.536
0.781	0.1860	0.590	0.517
1.644	0.1732	0.875	0.481
		1.079	0.462
		1.915	0.410

Incidentally, this argument suggests the presence of a linear term in equation 1 which could become visible at low chain electrolyte concentrations. Unfortunately, the 1.5% salt was not soluble in nitromethane. However, the data in methyl ethyl ketone clearly show a tendency for a linear increase in z with C once the minimum is passed. No direct comparison is possible because the two solvents differ so widely in dielectric constant, and ion association at a given salt concentration is therefore very different.

We finally turn to a consideration of the effects of other electrolytes on the hydrodynamic properties of the polyelectrolytes. It has been shown (1) that excess simple electrolytes such as potassium bromide will eliminate the sharp rise of reduced viscosity at low polyelectrolyte concentration and eventually convert the z - C curves into linear plots. It seemed of interest to determine whether a similar behavior would be found in nonaqueous systems. Tetrabutylammonium bromide is a simple one-one electrolyte soluble in a variety of nonaqueous solvents such as nitromethane. As can be seen from the data of Tables X-XII and the example shown in Figure 7, a complete parallel between aqueous and nonaqueous systems is found. A small amount of added electrolyte produces a maximum in the viscosity curve

TABLE XIII. Empirical Constants for Copolymer Salts in Nitromethane

No.	D	B/A	B	A
6.6	0.11	8.85	20.6	2.33
13	0.14	3.88	27.2	7.00
26	0.23	2.60	-	-
26[a]	0.18	3.26	20.4	6.25
26[b]	0.15	7.60	-	-
58	0.15	2.48	38.2	15.4
90	0.18	2.42	27.9	11.6

[a] 83-17 nitromethane-dioxane

[b] 60-40 nitromethane-dioxane

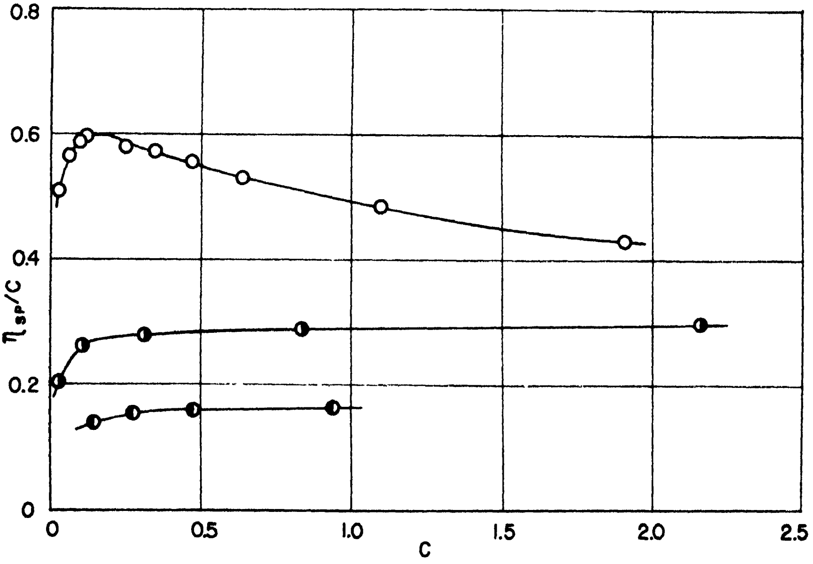

Fig. 7. Effect of added simple electrolyte (Salt 90, Table X).

and an excess converts it into an approximately linear curve. In 0.1 N tetrabutylammonium bromide solution, for example, the reduced viscosity is about the same as that of the parent polymer. The high concentration of negative ions increases the association of bromide ions with the polyelectrolyte by a mass action effect and thus nullifies electrostatic repulsion within the chain, permitting it to curl up more tightly, and the lower space requirement is mirrored in the lower viscosity observed.

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Synopsis

A series of copolymers, of 4-vinylpyridine and styrene, covering the range 1.5 to 100% vinylpyridine were prepared in 20% toluene solution at 80°. Strong electrolytes were then made by the addition of n-butyl bromide in nitromethane solution. The salts with high vinylpyridine content were soluble in water, alcohols, nitromethane, and other polar solvents. Viscosities of the parent copolymers in methyl ethyl ketone were in the range 0.15–0.20; osmotic pressures

gave molecular weights in the range 50,000-80,000. The polyelectrolytes in nitromethane and nitromethane-dioxane mixtures gave viscosity-concentration curves which were strongly concave upwards: at 1 mg./100 cc., the reduced viscosity of the salt of polyvinylpyridine in nitromethane was 6.0. The salts of the different copolymers did not differ much in their viscosities at concentrations above a few tenths of a gram per 100 cc., a fact which shows a high degree of ionic association; only as zero concentration is approached, can the detailed polymer structure be seen. The extent of association at a given concentration is controlled by the amount of vinylpyridine in the copolymer and by the dielectric constant of the solvent. Addition of simple one-one electrolytes, such as tetrabutylammonium bromide, suppresses the electrostatic increase in viscosity which otherwise appears at low concentrations. The following empirical equation:

$$\eta_{sp}/C = A/(1 + B\sqrt{C}) + D$$

was found to fit the data for the different systems studied. The constant A depends on copolymerization ratio and probably on molecular weight; it is a measure of the extent to which the polymer coil can spread out at infinite dilution as a consequence of the intramolecular Coulomb repulsion between charges attached to the chain. It is roughly several orders of magnitude larger than the intrinsic viscosity of the parent polymer. The constant B is a measure of the electrostatic forces and increases with decreasing dielectric constant of the solvent.

Résumé

Une série de copolymères de la 4-vinylpyridine et du styrène ont été préparés en solution toluénique à 80°, avec des teneurs en vinylpyridine variant de 1.5 à 100%. Des électrolytes forts en ont été faits par addition de bromure de butyle normal en solution dans le nitrométhane. Les sels, contenant beaucoup de vinylpyridine, sont solubles dans l'eau, l'alcool, le nitrométhane, et les autres solvants polaires. Les viscosités des copolymères d'origine, mesurées dans la méthyléthylcétone, s'élèvant à 0.15-0.20; les pressions osmotiques indiquent des poids moléculaires de 50,000-80,000. Les polyélectrolytes, dissouts dans le nitrométhane et dans le mélange nitrométhane-dioxane, donnent des courbes, viscosité/concentration, fortement concaves vers le haut;à 1 mgr./100 cc., la viscosité réduite du sel de polyvinylpyridine s'élève à 6.0 en solution dans le nitrométhane. Les sels des différents copolymères ne diffèrent que peu dans leurs viscositiés aux concentrations supérieures à quelques décigrammes par 100 cc., ce qui prouve un degré éléve d'association ionique. Uniquement au concentration tendant vers zéro, on se rapproche de la structure du polymère particulier considéré. L'importance de cette association à une concentration déterminée dépend de la quantité de vinylpyridine présente dans le copolymère, et de la constante diélectrique du solvant. L'addition d'électrolytes (monovalents un-un) tel que le bromure de tétrabutylammonium, supprime l'accroissement électrostatique de la viscosité, qui d'autre part apparait aux faibles

concentrations. L'équation suivante répond aux mesures effectueés sur les systèmes considérés (formule empirique):

$$\eta_{sp}/C = A/(1 + B\sqrt{C}) + D$$

La constante A dépend de la copolymérisation de départ et probablement du poids moléculaire; c'est une mesure de la limite à laquelle le polymère, ramassé sur lui-même, peut s'étendre à dilution infinie, par suite de la répulsion intramoléculaire entre les charges coulombiennes attachées à la chaîne. En général, sa valeur est de plusieurs ordres de grandeur supérieurs à la viscosité intrinsèque du polymère d'origine. La constante B est une mesure des forces électrostatiques et s'accroît avec une diminution de constante diélectrique du solvant.

Zusammenfassung

Eine Reihe von Mischpolymerisaten von 4-Vinylpyridin und Styrol mit einem Vinylpyridin Inhalt zwischen 1.5 und 100% wurden als 20% Lösungen in Toluol hergestellt und dann in starke Elektrolyte durch Zugabe von n-Butylbromid in Nitromethan Lösung verwandelt. Die Salze mit hohem Vinylpyridin Gehalt waren in Wasser, Alkohol, Nitromethan und anderen polaren Lösemitteln löslich. Viskositäten der Ausgangspolymerisate in Methyläthylketon lagen zwischen 0.15 und 0.20, osmotische Drucke ergaben Molekulargewichte zwischen 50,000 und 80,000. Die Polyelektrolyte ergaben in Nitromethan und Nitromethan-Dioxan Mischungen Viskosität-Konzentrationskurven die stark nach obenzu gebogen waren: Bei 1 Milligram in 100 cc. war die innere Viskosität des Salzes von Polyvinylpyridin in Nitromethan 6.0. Die Salze der verschiedenen Mischpolymerisate underschieden sich wenig in ihren Viskositäten bei Konzentrationen die einige Zehntel Gram in 100 cc. überschritten, was auf hohe Ionenassozierung hinweist; nur als man einer Null-Konzentration nahekommit, können Feinheiten der Polymerstruktur beobachtet werden. Das Ausmoss der Assoziation bei einer gegebenen Konzentration ist von der Menge von Vinylpyridin in Mischpolymerisat und von der Dielektrischen Konstante des Lösemittels abhängig. Zugabe einfacher ein-ein wertiger Elektrolyte wie zum Beispiel Tetrabutylammonium Bromid drückt die elektrostatische Viskositäts-Erhöhung, die sonst bei niedrigen Konzentrationen in Erscheinung tritt, herab. Die folgende empirische Formel:

$$\eta_{sp}/C = A/(1 + B\sqrt{C}) + D$$

beschreibt gut die Ergebnisse in den verschiedenen untersuchter Systemen. Die Konstante A ist vom Mischpolymerisations-Verhältniss und wahrscheinlich auch vom Molekulargewicht abhängig; sie ist ein Mass der Ausdehnbarkeit der Polymerenkette bei unendlicher Verdünnung durch innermolekulare Coulombsche Repulsionskräfte zwischen den an die Kette gebundenen Ladungen. Sie ist einige Grössenordnungen grösser als die innere Viskosität des Ausgangspolymerisates. Die Konstante B ist ein Mass elektrostatischer Kräfte und steigt mit sinkender dielektrischer Konstante des Lösemittels an.

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Polyelectrolytes. IV. Conductance of n-Butyl Bromide Addition Compounds of 4-Vinylpyridine-Styrene Copolymers in Nitromethane-Dioxane Mixtures *

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INTRODUCTION

Copolymers of styrene and vinylpyridine are very much like polystyrene in their behavior, except for obvious solubility differences due to the polarity of the pyridine groups. By adding alkyl halides such as n-butyl bromide to the copolymers, polyelectrolytes are obtained, whose properties differ markedly from those of the neutral parent polymers. In the previous paper of this series, we described the hydrodynamic behavior of these synthetic polyelectrolytes, and showed how the presence of ionic groups on the polymer chain gave rise to a characteristic increase of reduced viscosity with increasing dilution.

In this paper, we present the results of an investigation of the conductance of the same salts in solvents covering the range of dielectric constant from 2.2 to 40. The code numbers (1) of the salts are those used in the preceding paper and give in round numbers the mole percent F of vinylpyridine in the parent polymer. Conductances were measured for the most part on the Shedlovsky (2) bridge; the Schering bridge (3) was used for the measurements in dioxane where the resistances were quite high. With the Shedlovsky bridge, an Erlenmeyer cell (4) with bright platinum electrodes 2.5 x 1.7 cm. spaced 3 mm. apart was used; its constant was 0.05359. For the high resistances, a platinum test-tube cell (5) with constant 0.00696 was used. All measurements were made at 25.00°.

RESULTS

The experimental results are given in Tables I-VII. Concentrations c are calculated as stoichiometric equivalents of bromide per liter rather than as grams solute per deciliter solution (C scale) as is conventional for most polymer work. We prefer the c scale for the

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presentation of conductance data because it is a direct measure of the ionic content of the solution, and it is the ions which carry the current. It must then be remembered that a given value of c corresponds to a weight concentration C which increases as F, the mole fraction of vinylpyridine decreases, because a given number of pyridonium groups carry increasingly more electrolytically inert styrene groups with decreasing F. The relation between the two concentration scales is given by:

$$c = 10CF/[S + (P + B - S)F] \quad (1)$$
$$= 10CF/(104.15 + 137.02F) \quad (1')$$

where S, P, and B are the molecular weights of styrene, vinylpyridine, and butyl bromide, respectively. Equivalent conductances Λ are then calculated by the definition:

$$\Lambda = 1000\ \kappa/c \quad (2)$$

where κ is the observed specific conductance of the solution corrected for solvent conductance.

Our original program of research was to cover the whole range of copolymer compositions in solvents covering as wide a range of dielectric constants as possible. It soon became evident, however, that only salts of styrene-rich copolymers could be studied in solvents of low dielectric constant, because the pyridine-rich compounds were insoluble; similarly, in solvents of high dielectric constant, only the pyridine-rich salts were soluble. We are at present investigating other polyelectrolytes which may have a wider range of solubility. Furthermore, adsorption effects were especially troublesome in solvents of low dielectric constant, and the conductance changed with time. The data given in Table I (dioxane) and Table II (ethylene dichloride) are, therefore, only to be considered as preliminary approximate values. In mixtures of dioxane and nitromethane, however, conductances were constant and reproducible, and adsorption errors could be eliminated with no more than the usual amount of care. We therefore feel that the data in the range $16 \leqslant \varepsilon' \leqslant 40$ are reasonably reliable. The nitromethane-dioxane mixtures used had the following dielectric constants at 25°: weight percent nitromethane 40, $\varepsilon' = 16.0$; 60%, 23.1; 83%, 32.1; 100%, 39.4.

In most cases, several runs were made on each system. Both concentration and dilution runs were made; in the first, solid salt or salt solution is added to solvent in the conductance cell and here adsorption errors tend to make the conductance low in the dilute range; in the second, successive portions of solvent are added to a starting solution in the cell and here desorption errors tend to make the conductance high in the dilute range. Solvent conductances were always checked at frequent intervals and are given in the tables at the head of each run. Purification of solvents has been described in the previous paper. For nitromethane, the conductance varied from 1.0 to 15.0×10^{-7}, depending on how long it stood after distillation from phosphorous pentoxide. Corrections for solvent conductance were in general held to a maximum of 5% and were usually much smaller; a batch of solvent was redistilled when its conductance became too high.

TABLE I. Conductance of Salt 1.5 in Dioxane.

$c \times 10^5$	$\Lambda \times 10^5$	$c \times 10^5$	$\Lambda \times 10^5$
$\kappa_0 = 2.4 \times 10^{-14}$		$\kappa_0 = 4.8 \times 10^{-14}$	
1.27	11.30	0.332	25.5
3.96	5.10	0.919	15.18
14.00	2.17	2.62	7.25
$\kappa_0 = 10.2 \times 10^{-14}$		9.21	3.06
51.4	1.629	22.7	1.88
158.1	1.242		
450.0	0.975		

TABLE II. Conductance of Salt 6.6 in Ethylene Dichloride.

$\kappa_0 = 1.57 \times 10^{-10}$

$c \times 10^6$	$\Lambda \times 10^6$
1.12	16.35
4.95	12.41
29.4	8.91
126.2	6.30
468	4.15

TABLE III. Conductance of Salt 1.5 in 40 : 60 Nitromethane-Dioxane.

$\kappa_0 = 1.1 \times 10^{-7}$

$c \times 10^4$	$\Lambda \times 10^4$
0.331	27.7
0.809	24.9
2.27	20.4
6.11	15.81
12.41	12.81
26.3	9.96

TABLE IV. Conductance of Salt 6.6 in Nitromethane-Dioxane Mixtures.

$c \times 10^4$	$\Lambda \times 10^4$	$c \times 10^4$	$\Lambda \times 10^4$
40:60 CH_3NO_2-$C_4H_8O_2$		60:40 CH_3NO_2-$C_4H_8O_2$	
$\kappa_0 = 1.0 \times 10^{-7}$		$\kappa_0 = 1.4 \times 10^{-7}$	
0.556	14.70	0.326	38.5
1.010	13.55	0.733	34.4
2.03	12.11	1.880	30.1
4.30	10.62	4.99	26.2
7.10	9.63	11.90	23.1
11.81	8.73	23.6	20.9
27.5	7.35		

TABLE V. Conductance of Salt 26 in Nitromethane-Dioxane Mixtures.

$c \times 10^4$	$\Lambda \times 10^4$	$c \times 10^4$	$\Lambda \times 10^4$
40:60 CH_3NO_2-$C_4H_8O_2$		60:40 CH_3NO_2-$C_4H_8O_2$	
$\kappa_0 = 1.1 \times 10^{-7}$		$\kappa_0 = 2.3 \times 10^{-7}$	
1.663	2.96	0.478	14.51
4.13	2.67	1.050	13.18
10.89	2.32	2.23	11.98
25.1	2.03	4.75	10.88
83:17 CH_3NO_2-$C_4H_8O_2$		$\kappa_0 = 11.7 \times 10^{-7}$	
$\kappa_0 = 8.3 \times 10^{-7}$		8.81	9.30
4.40	23.1	15.31	8.90
8.37	21.6	39.0	8.23
19.60	19.9	86.8	7.75
40.2	18.8		

DISCUSSION

Dependence of Conductance on Concentration

Little more than a casual glance at the data of Table I-VII is needed to show that the conductance of the polysalts shows no similari-

TABLE VI. Conductance of Salt 90 in Nitromethane.

$c \times 10^4$	$\Lambda \times 10^4$	$c \times 10^4$	$\Lambda \times 10^4$
$\kappa_0 = 1.9 \times 10^{-7}$		$\kappa_0 = 1.4 \times 10^{-7}$	
0.631	14.87	9.56	10.11
1.552	13.18	23.8	9.03
5.17	11.04	47.6	8.30
11.30	9.95	88.7	7.72
27.4	8.87	199.1	7.14

ty in its concentration dependence to that characteristic of ordinary electrolytes. The latter, in solvents of low dielectric constant, approach linearity at low concentrations with a slope of minus one-half on a log-log scale (6), while our data for Salt 1.5 in dioxane show a distinct curvature. In solvents of higher dielectric constant, ordinary strong electrolytes give S-shaped conductance curves (7), which approach a predictable limiting tangent (8) at low concentrations on a $c^{1/2}$ scale; and in solvents of high dielectric constant, the conductance curves lie quite near the limiting tangent (8) at low concentrations. The data of Table III-VII, on the other hand (except for Salts 1.5 and 6.3 in the 40:60 nitromethane-dioxane mixture), all give linear log-log plots with a slope of -0.13, and are strongly concave-upward at low concentrations on the $c^{1/2}$ scale with no obvious tendency to approach a limiting value.

Examples are shown in Figures 1 and 2, where logarithm of equivalent conductance is plotted against logarithm of concentration c (stoichiometric equivalents of bromide per liter). Both for different copolymers in nitromethane and for the same salt (No. 26) in different solvents, the data lie on parallel straight lines whose slopes average to -0.13. We hasten to emphasize that we are not suggesting that the conductance function is:

$$\Lambda = kc^{-0.13} \tag{3}$$

because it is well known that practically any monotone function may be interpolated linearly on a log-log scale over a limited range of the variables. The fact that so many different systems (including even the 1.5 salt in dioxane in the concentration range $10^{-4} \leqslant c \leqslant 10^{-2}$) satisfy equation 3 does, however, suggest that a general (as yet unknown) conductance function for polyelectrolytes exists.

Two kinds of ions are naturally present, cations and anions, and the total conductance is made up of contributions of each species. For a given copolymer salt in a given solvent, we may expect the contributions of cations and ions to vary with concentration for several reasons.

Let us first consider the spatial distribution of ions at concentrations so low that there is negligible geometrical interference (9) between the large cations. Then we will have an approximately uniform distribution of cations, with some negative counter ions distributed in the solvent between the large cations and some within the average volume "occupied" by the cations. The distribution of the anions will thus not be uniform: if we choose an origin at the "center" of a reference cation coil, the density, ρ_1 of anions will be high within the average radius, R, of the coil (the zone of bound anions) due to the high concentration of positive charge always present in the polyion, and then there will be a decrement of anion density in the range

TABLE VII. Conductance of Copolymer Salts in Nitromethane.

$c \times 10^4$	$\Lambda \times 10^4$	$c \times 10^4$	$\Lambda \times 10^4$
Salt 6.3		Salt 58	
0.636	75.0	0.770	22.70
1.386	70.1	2.17	19.58
2.26	66.5	4.80	17.52
3.37	64.0	8.91	15.48
5.41	61.5	10.78	15.84
8.15	58.5	24.0	14.59
16.91	53.3	38.2	13.18
25.9	50.5	85.0	12.19
35.2	48.5	166.8	11.40
Salt 26		Salt 78	
0.208	50.0	0.781	15.83
0.525	45.4	1.692	14.30
1.514	39.8	4.24	12.78
3.56	35.8	8.88	11.55
4.68	34.1	13.85	11.41
9.10	32.1	26.2	10.22
10.65	31.6	33.0	10.06
14.51	31.2	59.0	9.12
23.6	29.6	109.1	8.61
38.7	28.5	202.5	8.45
68.5	27.2		

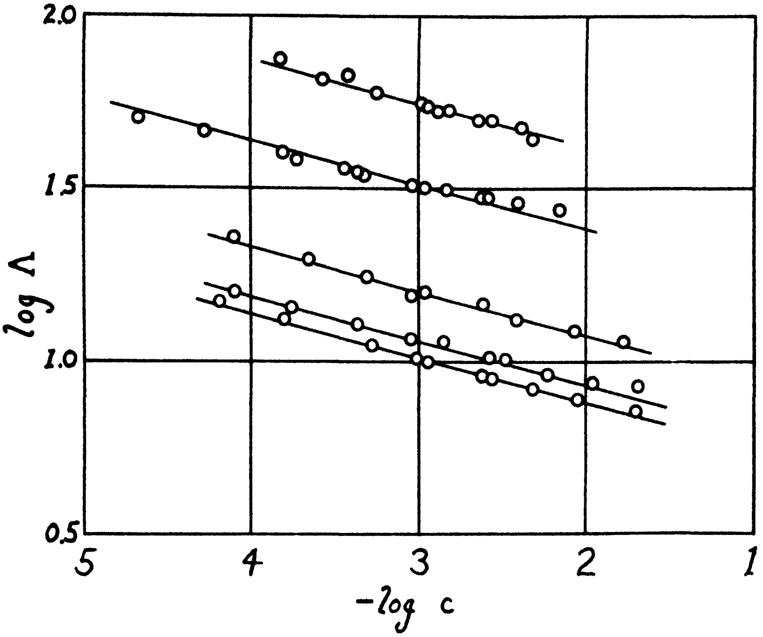

Fig. 1. Conductance of Salts 6.6 (top curve), 26, 58, 78 and 90 (bottom curve) in nitromethane.

of distances up to several times R to an average space charge density ρ_2, characteristic of the cation-free space between polyions. If we measure distances along a coordinate connecting two polyions, the

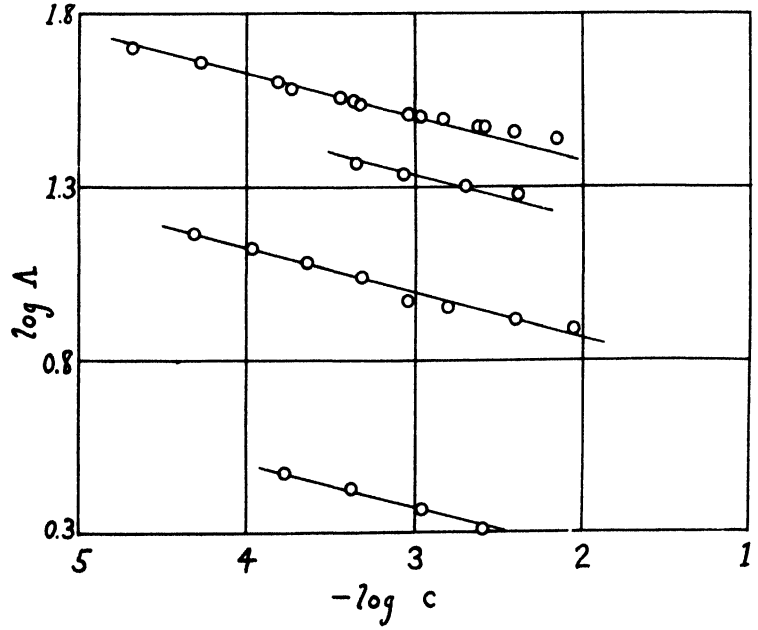

Fig. 2. Conductance of Salt 26 in nitromethane (top curve), 83:17 nitromethane-dioxane, 60:40 nitromethane-dioxane, 40:60 nitromethane-dioxane (bottom curve).

anion density should then have approximately the contour shown in Figure 3. The distances r and d will increase with dilution: the former is the average cation-cation center-to-center distance and the latter is the distance over which bromide ions are far from cations on a scale of distances measured in units equal to R. The anions in the range d (the zone of free anions) will have approximately their normal mobility and their relative concentration will increase with dilution, so we expect the anion conductance to increase with dilution. The anions in the range R around the center of a cation coil will be carried along with the cation and will not contribute to conductance; their relative amount will decrease with dilution as their probability of escape from the cation field is increased. The anions in the range between $(r - d)/2$ and R (the screening zone) will partly be carried along with the cation, or, perhaps more accurately stated, their mobility will be decreased by a strong electrophoretic term. The contribution of the cations will increase with dilution because as more and more anions escape the net charge on the cation and hence its mobility will increase. At the same time, however, escape of anions will decrease the mobility of the cation by increasing its friction coefficient: mutual repulsion between newly unpaired positive centers within the coil will cause the latter to expand. Since the first effect will be proportional to Z, the net instantaneous charge on the cation, and the second to a fractional power of Z, the resultant effect will be an increase of mobility, and hence of conductance of the cation, with dilution. Interaction of all the factors mentioned above will lead to a conductance function $\Lambda = \Lambda(c)$ for the polyelectrolytes. In making a calculation based on this picture, it must be remembered that there is a dynamic exchange equilibrium between anions in the bound zone, the screening zone, and the free zone.

Considering next the distribution at higher concentrations, we would expect that the free zone will cease to exist when the screening zones of neighboring cations start to overlap. This region of concentration will be analogous to the critical range[10] of concentration found for one-one electrolytes, where the distinction between free and associated ions breaks down. In addition to suggesting a theoretical approach to the problem, these considerations also suggest the experiment of measuring the conductance of mixtures of polyelectrolytes and simple electrolytes: the conductance of the mixture should be less than the sum of the conductances of the component because the net charge on polycation would be strongly reduced by an excess of anions over the stoichiometric equivalent.

Dependence of Conductance on Copolymer Ratio

Somewhat similar qualitative conclusions concerning association may be drawn from the data shown in Figure 1 for the conductances of the different copolymers in nitromethane, with dielectric constant $\varepsilon' = 39.4$. It may first seem surprising that at a given salt concentration the equivalent conductance increases with decreasing pyridine content. Certainly at infinite dilution, we would expect just the reverse to hold. Since we are unable to extrapolate our conductance data to zero concentration, we are forced to consider the data in the finite experimental range of concentration, approximately $10^{-4} < c < 10^{-2}$. It should first be pointed out that reversal is not a viscosity effect: at c = 10^{-3} for example, C increases from 0.025 g./100 cc. to 0.172 on going from Salt 90 to Salt 6.6; i.e., for fixed equivalent bromide concentration, the weight concentration increases with decreasing pyridine content and hence any mass viscosity effect would act in the opposite direction to that observed as far as conductance correction goes. As a matter of fact, at c = 10^{-3}, the relative viscosity of the different copolymer salts varies from 1.06 to 1.10, a change negligible compared to the fivefold change in equivalent conductance that is under discussion.

The decrease in conductance (at a given concentration) with increasing pyridine content was observed in three solvents: Salts 1.5, 6.6, and 26 in 40:60 nitromethane-dioxane, Salts 6.6 and 26 in 60:40 nitromethane-dioxane and Salts 6.6, 26, 58, 78, and 90 in nitromethane. With degrees of polymerization of the order of 700, the average chains contain from about 50 to 600 potential ionic groups in the series measured in nitromethane. These data may best be compared if we plot equivalent conductance at a fixed concentration (10^{-3} normal was chosen for Figure 4) against F, the mole percent of vinylpyridine in the parent polymer, as is shown in Figure 4. At very low vinyl pyridine content, we would expect the transference number and mobility of the cation to be nearly zero because the few pyridonium groups in a chain would have to drag a lot of nonelectrolytic polystyrene chain through the solvent. We therefore have extrapolated the curve to 58.0, the conductance of the bromide ion at 10^{-3} normal in nitromethane.* The fact that the total conductance increases rather than decreases as we go from high to low pyridine content signifies that ionic association increases with increasing pyridine content. The pyridonium groups are tied to the polymer chain, and, therefore, the total positive charge density in the polycation increases with increasing F; hence more bromide ions are drawn into the sphere of the cation and its mobility is kept from increasing in proportion to the number of ionic groups, while simultaneously the relative concentration of free bromide ions is decreased. On the other hand, at fixed equivalent bromide concentration, the mass concentration of polymer decreases with increasing F, which increases average intercationic distances, an effect that probably tends to increase free bromide ion concentration. Since the total conductance decreases with increasing F, we conclude that the effect of increased association due to increased charge density within the coil predominates.

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*This value was obtained as follows. Witschonke and Kraus (J. Am. Chem. Soc., 69, 2472, 1947) give 21.6 as the limiting mobility of the bromide ion in nitrobenzene, a solvent with viscosity 1.811 cp. Using Walden's rule (limiting mobility inversely proportional to viscosity), we find $\lambda_\infty(\mathrm{Br}^-) = 63.0$ in nitromethane with $\eta = 0.6203$ cp. The Onsager coefficient in nitromethane is 162.4, whence we find 57.9 as the bromide ion conductance at 10^{-3} normal in nitromethane. Alternatively, Walden and Birr (Z. physik. Chem., A163, 263, 1933) give 101.3 as the conductance of tetramethylammonium bromide in nitromethane. At the same concentration, tetrabutylammonium and tetraethylammonium picrates have conductances of 71.9 and 86.3, respectively, whence we estimate the conductance of tetrabutylammonium bromide to be 101.3-(86.3 - 71.9) = 86.9 at 10^{-3} normal. Using Witschonke and Kraus's values for the limiting conductances of the bromide ion and of tetrabutylammonium bromide in nitrobenzene, we obtain 21.6/33.5 = 0.645 as the transport number of the bromide ion. Neglecting its change with concentration and assuming it to be the same in nitrobenzene and nitromethane, we find 0.645 (86.9) = 56.0 as the conductance of the bromide ion at 10^{-3} normal nitromethane. We used the average of these two calculated values to locate the point at F = 0 on Figure 4.

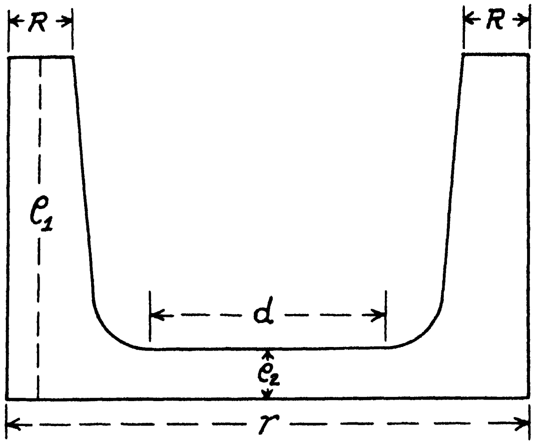

Fig. 3. Anion density as a function of distance.

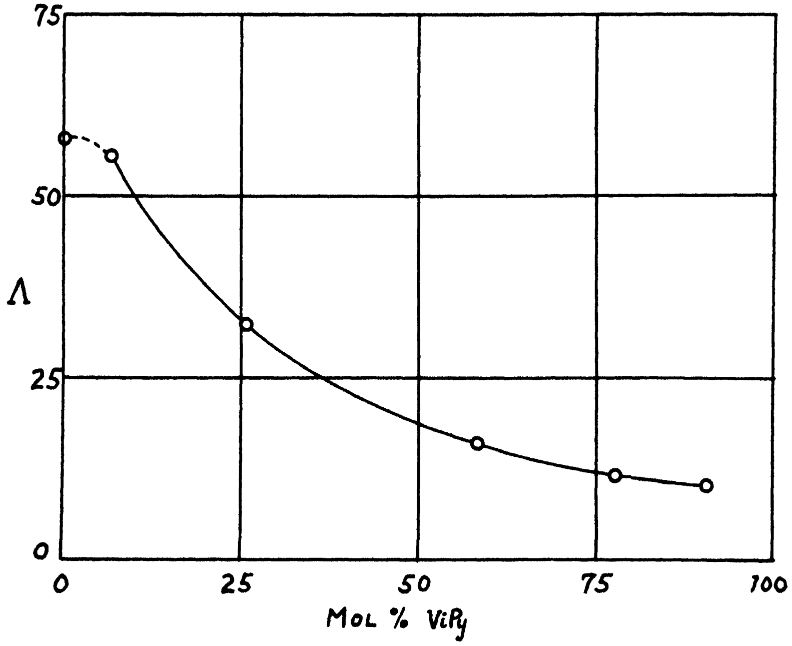

Fig. 4. Dependence of conductance on copolymer ratio.

The curve as a whole is S-shaped; since we would expect the decrease of free bromide ion concentration to be monotone, we must look for the explanation of the concave-downward section of the curve near $F = 0$ in the contribution of the cation. Near $F = 0$, we would expect the mobility of the cation to increase from zero with increasing F until the effects of increased association cancelled the potential increase; in other words, the contribution of the cation is probably represented by a concave-downward curve with strongest curvature near $F = 0$. The sum of this plus the concave-upward curve for the bromide ion conductance would then account for the shape of the resultant curve of Figure 4.

Dependence of Conductance on Dielectric Constant

In every case investigated, the conductance of a given salt at a given concentration decreased with decreasing dielectric constant of the solvent. An example is shown in Figure 2 for Salt 26 in a series of solvents. The viscosity change is negligible compared to the decade change in conductance in going from 40:60 nitromethane-dioxane to nitromethane, and we must ascribe the change in conductance to a consequence of the change in dielectric constant ε' from 16.0 to 39.4. If we assume that a certain fraction of the bromide ions are electrostatically bound to (or in) the polyions and therefore not free to contribute to conductance, we would expect this fraction to increase with decreasing dielectric constant of the solvent medium—other variables being fixed—because Coulomb potential energy varies as $1/\varepsilon'$.

In a theoretical treatment of the problem, the electrostatic energy will appear as a ratio to thermal energy in a Boltzmann exponential function which will measure the fraction of ions free to carry the current. Since equivalent conductance is proportional to the relative amount of unassociated charges, we might expect a linear relationship between the logarithm of equivalent conductance and reciprocal dielectric constant. As shown in Figure 5 for Salts 6.6 and 26 nitromethane-dioxane mixtures at $c = 10^{-3}$ normal in all systems, the data do indeed give linear plots. The two lines apparently extrapolate to the same limit at infinite dielectric constant; this may be merely coincidence. Considered only as an interpolation plot, however, Figure 5 shows unambiguously that ionic association under the influence of Coulomb forces must be considered for polyelectrolytes. This is in agreement with our findings (11) for Salt 90 in water-ethanol mixtures.

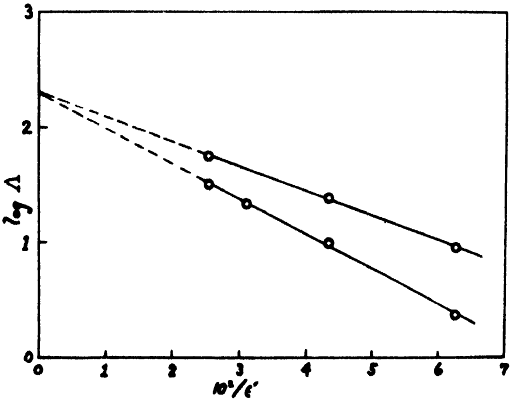

Fig. 5. Dependence of conductance on dielectric constant (Salt 6.6, top curve; Salt 26, bottom curve).

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Synopsis

The conductance of a series of salts made by the addition of n-butyl bromide to 4-vinylpyridine-styrene copolymers (1.5 to 90 mole per cent vinylpyridine) has been measured in dioxane ($\varepsilon' = 2.2$), ethylene dichloride ($\varepsilon' = 10.2$), and a series of nitromethane-dioxane mixtures ($16.0 \leqslant \varepsilon' \leqslant 39.4$). Three independent arguments deduced from the data show that ionic association under the influence of interionic electrostatic forces must occur in solutions of polyelectrolytes in such a way that a certain average fraction of the counter ions accompany the large polycation and contribute nothing to conductance. First, the conductance at fixed copolymer composition and fixed salt concentration decreases with decreasing dielectric constant of the solvent medium. Second, at a given counter ion concentration in a given solvent, the conductance decreases with increasing pyridonium content of the chain. Third, for a given salt and solvent, the conductance decreases with increasing salt concentration at a rate much slower than that characteristic of simple electrolytes.

Résumé

Les conductivités d'une série de sels, préparés par addition de bromure de butyle-normal aux copolymères de la 4-vinylpyridine et du styrène (de 1.5 à 90% moles de vinylpyridine), ont été mesurées en solution dans le dioxane ($\varepsilon' = 2.2$), dans le dichloréthylène ($\varepsilon' = 10.2$), et dans des mélanges variés de nitrométhane et dioxane ($16.0 \leqslant \varepsilon' \leqslant 39.4$). Trois arguments indépendants, déduits des résultats, prouvent que l'association ionique résulte, dans ces solutions de polyélectrolytes, de l'action de forces électrostatiques interioniques, et de telle façon, que une certaine partie des ions de signe contraire accompagne le polycation, et de ce fait, n'intervient pas dans la conductivité. Premièrement, la conductivité pour une composition déterminée du copolymère et pour une concentration déterminée de sel, décroît si on diminue la constante diélectrique du milieu-solvant. Secondement, à une concentration déterminée d'ions de signe contraire dans un certain solvant, la conductivité décroît avec la teneur en fragments pyridiniques de la chaîne. Troisièmement

pour un sel et un solvant déterminés, la conductivité décroît, par augmentation de la concentration en sel, à une vitesse notablement inférieure à celle caractéristique pour les électrolytes simples.

Zusammenfassung

Es wird die Leitfähigkeit einer Reihe von Salzen die durch Addition von n-Butylbromid an 4-Vinylpyridin-Styrol Mischpolymere (1.5 bis 90 Mol-% Vinylpyridin) in Dioxan ($\varepsilon' = 2.2$), Äthylendichlorid ($\varepsilon' = 10.2$) und einer Reihe von Nitromethan-Dioxan Gemischen ($16.0 \leqslant \varepsilon' \leqslant 39.4$) gemessen. Aus den experimentellen Daten werden drei unabhängige Beweise dafür abgeleitet, dass in Lösungen von Polyelektrolyten Ionenassoziation unter dem Einfluss von zwischenionischen elektrostatischen Kräften stattfindet in solch einer Weise, dass ein gewisser durchschnittlicher Bruchteil der Gegenionen das grosse Polykation umhüllen und nicht zur Leitfähigkeit der Lösung beitragen. Diese Argumente sind die folgenden. Erstens, die Leitfähigkeit nimmt bei vorgegebener Kopolymerzusammensetzung und vorgegebener Salzkonzentration mit abnehmender Dielektrizitatskonstante des Lösungsmittels ab. Zweitens, die Leitfähigkeit nimmt bei vorgegebener Gegenionkonzentration in einem gegebenen Lösungsmittel mit Zunahme des Pyridoniumgehaltes der Kette ab. Drittens, die Leitfahigkeit nimmt für ein gegebener Salz und Lösungsmittel mit zunehmender Salzkonzentration viel langsamer als bei einfachen Elektrolyten ab.

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X-Ray Studies on the Crystallinity of Cellulose*

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INTRODUCTION

In an earlier paper (1) a method was given for the quantitative evaluation of the crystalline fraction in cellulose fibers from intensity measurements on x-ray diffraction pictures. This fraction was found to be equal within experimental error for cotton, cotton linters, flax, and ramie (0.70), and also for nine samples of regenerated cellulose (0.39) independent of their degree of orientation. The crystalline fraction in native wood pulp is slightly lower than in cotton and very much lower in bacterial cellulose. It was further shown that the figures obtained reasonably conform with those estimated from other physical constants (2).

The purpose of the present paper is to communicate further measurements extending the range of observed crystallinities from 0.08 to 0.70, and to discuss these in conjunction with the former ones.

METHOD

For the sake of clarity we shall briefly repeat the principle of our method (see Fig. 1). For its details and their justification see previous paper (1). A beam of copper radiation strictly monochromatized by reflection, limited by pinhole system P with an intensity I_O, is transmitted by cellulose O with intensity I, reduced by absorption, and then strikes the front of auxiliary miniature camera G (3) where a disk of an inorganic comparison substance is located. The latter produces a characteristic interference, I_C, on the film inside the miniature camera, which serves as a means for standardizing all exposures taken to equal intensity of the primary radiation I_O. Evidently, I_C is always proportional to I, it will also be proportional to I_O and to the intensity I_{hkl} of the cellulose spectrum on the film outside the minature camera, provided the dimensions and the density of the cellulose specimen O are kept vigorously constant. This has been achieved by the use of carefully prepared fiber pellets (consisting of fibers orientated at random) of constant weight and dimensions.

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*Contribution No. 54 from the Laboratory for Cellulose Research, Utrecht. See also page 145, this issue.

The absorption in the specimen is given by the equation:

$$I = I_0 \exp - \mu_m \rho d$$

where μ_m is the mass absorption coefficient of cellulose (7.78), ρ the density of the pellet, and d the irradiated thickness. (At the end of each exposure, the absorption, and hence the value of $\mu_m \rho d$, was measured as a control).

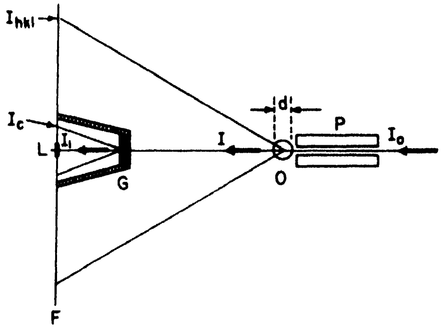

Fig. 1. Diagram of setup for exposures: P, pinhole system; O, isotropic fiber pellet; G, auxiliary miniature camera; F, film; I_c, comparison interference.

To standardize all exposures to equal intensity of the primary radiation the observed values of the cellulose spectrum, I_{hkl}, were divided by I_c. In the case of the cellulose powders referred to below, tablets were pressed and used instead of the pellets. After exposure, an absorption measurement was carried out in order to determine the value of $\mu_m \rho d$ of the tablet. The value of I_c was then corrected by multiplication with $\rho' d' / \rho d$.

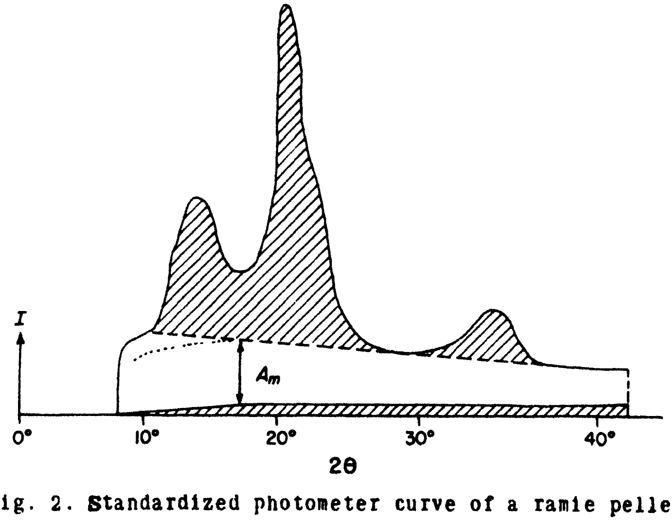

Fig. 2. Standardized photometer curve of a ramie pellet.

The method of evaluation is shown in Figure 2, where an example of a standarized radial photometer curve for a native fiber is given. (A reproduction of some actual photographs is given in

Plate I, see end of issue. The upper hatched area is taken as a relative measure of the crystalline fraction (integrated intensity of the coherent radiation selectively diffracted by the crystalline portion). It is indicated below as I_{cr}. The bottom hatched area is the correction for incoherent radiation (1). The dotted line represents the correction for the radiation scattered by the air in the camera. The height A_m of the broad background maximum above the lower hatched area was taken as a relative measure of the disordered fraction. As a control, the integrated intensity of the total diffracted radiation (corrected for air) was also determined. Its value was practically constant within experimental error.

As a basis for the computation of the absolute crystallinity, figures were taken from the average values of I_{cr} and A_m for five native fibers on the one hand, and for nine specimens of rayon on the other hand. (As previously stated, the single figures in each group were constant within experimental error.)

If x and y are the fractions of crystalline substance in the native fibers and rayon, respectively, then:

$$\frac{x}{y} = \frac{(I_{cr})_{native}}{(I_{cr})_{rayon}}$$

and:

$$\frac{1-x}{1-y} = \frac{(A_m)_{native}}{(A_m)_{rayon}}$$

for which x and y (allowing for small corrections owing to the difference in moisture content and the use of a plane film) were calculated to be:

$$x = 0.70 \pm 0.02 \qquad y = 0.39 \pm 0.03$$

With the aid of these two most reliable figures, the nomogram reproduced in Figure 3 was constructed. The results of the measurements on other cellulose specimens are also recorded.

RESULTS

All results are recorded in Figure 3. The oblique line in the nomogram represents the locus of the points of observation conforming to the standard points derived from the series of the five native and the nine rayon samples mentioned in the preceding section. The point for any specimen is found by plotting the observed A_m value against the observed I_{cr} value.*

In Table I the single determinations of I_{cr} and A_m are listed. The table is subdivided according to the type of spectrum that the samples exhibited. Further details on the nature of the samples 23-25 and 26-30 are given below.

In Figure 3 it is seen that the majority of the samples reasonably fit the oblique line, particularly those for which more than one determination was carried out. (The number of single observations is indicated by the figures in parentheses in Figure 3.) Moreover, for the two standard points (rayon and native), the spreading area of the single observations is indicated by a dotted line.

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*The idea of plotting the results in this form was suggested to the authors by Prof. W. Kast, Krefeld.

It is further seen that Fiber G is the only example of a rayon with a distinctly higher percentage crystallinity (53%) as compared to all other rayons investigated.* This striking fact must be due to causes other than the high orientation of this fiber, since Fortisan and the Lilienfeld rayon investigated also possessed the same, almost complete, orientation.

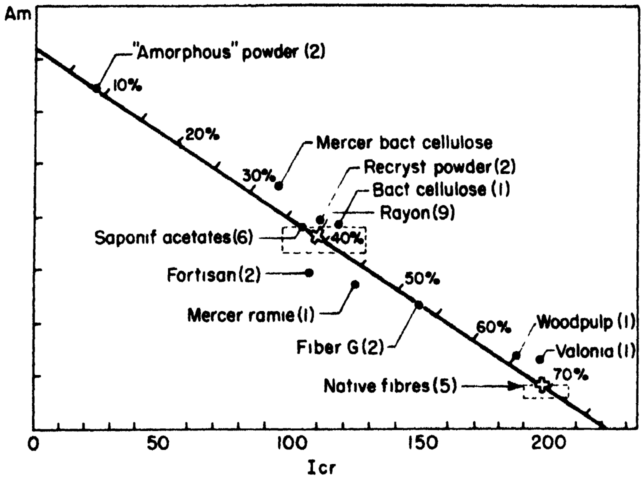

Fig. 3. Crystallinity nomogram for cellulose. A_m values are plotted against I_{cr} values. All experimental points ought to fall on the oblique line bearing a percentage crystallinity scale. Figures in parentheses indicate the number of parallel determinations for which the relevant points of observation are computed. In the cases of native fibers and rayon, the area of spreading of the single determinations is indicated by a dotted line.

The experiments with cellulose powders, (23)–(25), are also of considerable interest. The amorphous powder (23) was obtained by treating completely dry viscose rayon in a vibrating ball mill (Schwingmühle) for 21 hours as previously described (4), using a porcelain jar and 1/4-in. steel balls in order to reduce the ash content, which was only 1.77%. To follow the degree of destruction of lattice order reached, x-ray test pictures of the powder were taken and its heat of wetting was determined. The sample finally investigated represents the optimal result that could be obtained. It showed a heat of wetting of 31.7 cal./g., and possessed a residual crystallinity of 8-9% according to Figure 3. In Figure 4 its standardized photometer curve is given together with those of a rayon sample and of native ramie fibers. Plate I gives the reproductions of the actual x-ray photographs of the three samples. (Here the trace of the miniature camera and the comparison interference are seen in the central part of the pictures.) In Figure 4 it is seen that the background rises as the percentage crystallinity comes down. (The background curves separating the

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*The authors are indebted to Dr. A. F. Smith of du Pont's Experimental Station, Wilmington, Delaware, for kindly providing a sample of this interesting new fiber.

"crystalline" radiation from the diffuse background are indicated by dotted lines.) The "amorphous" powder shows a small and rather broad residual peak in the neighborhood of the 002 line.

A part of the "amorphous powder" was allowed to recrystallize by contacting it with hot water (4). The recrystallized product was dried and its crystallinity determined. It appeared to be quite near that of rayon (falling near the area of spreading of the latter in Figure 3.)

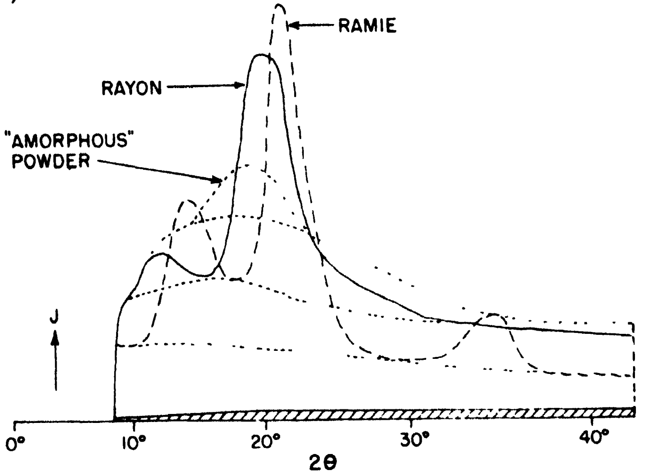

Fig. 4. Standardized photometer curves.

The heat of wetting of the completely dried recrystallized powder was found to be 19.9 cal./g. (in good conformity with the previously reported figure of 20.0 cal./g.). The corresponding value for rayon is 22 cal./g. The difference between the heats of wetting of the "amorphous" powder and that of rayon, amounting to 10 cal./g. or 1.62 kcal./mole, must represent the heat of crystallization of the fraction 0.39 - 0.09 = 0.30 of the material (4). This would mean that the molar heat of recrystallization of cellulose is equal to 1.62/0.30= 5.4 kcal. Since the heat of recrystallization of β-glucose as reported in literature is 5.5 kcal./mole and the corresponding value for cellulose may be expected to lie very near this figure, the result obtained may be considered as a valuable support of the x-ray results.

The saponified cellulose acetates (samples 26-30 in Table I) were all prepared from Setilose, a commercial acetate rayon, containing about 2.5 acetyl groups per glucose residue. The x-ray picture of this rayon was rather vague; its photometer curve is reproduced in Figure 5 (upper). It was taken from a "randomized pellet." If this product is heated for 30 minutes in a closed vessel with methanol at 100°C., it shows a kind of recrystallization-the x-ray picture now being sharper and exhibiting more lines. See photometer curve in Figure 5 (lower). Similar photographs were previously obtained by Fuller and Baker on "quenched" and "recrystallized" cellulose esters, polyamides, and other polymers. Since it seemed of interest to determine whether such samples yield a different degree of crystallization after saponification to cellulose, this item was included in Table I. However, no difference in percentage crystallinity could be detected within experimental error.

Using 3 N ammonia as a saponifying agent at 100°C., the saponified product appeared to consist of a mixture of cellulose II and cellulose IV. The proportion of cellulose IV decreases as the saponification temperature is lowered. At 40°C. and below, pure cellulose II is obtained. The same was found to apply to 0.2 N sodium hydroxide as a saponifying agent. Surpisingly, with 0.2 N barium hydrox-

TABLE I. Values of I_{cr} and A_m as Derived from Standardized Intensity Measurements (in Arbitrary Units).

Specimen	I_{cr}	A_m
Spectrum Cellulose I		
(1) Standard cotton	195	28
(2) Ramie (purified and bleached)	207	26
(3) Ramie (purified and bleached)	195	28
(4) Cottonine (flax).	203	28^5
(5) Cotton linters (mfgd. for viscose process).	180	28
Average	198 ± 5	28 ± 0.5
(6) Sulfite wood pulp from spruce	188	34
(6a) Valonia cell wall.	197	29^5
(7) Bacterial cellulose (*Bacterium xylinum*)	119	58^5
Spectrum Cellulose II		
(8) Viscose staple fiber (AKU-Arnhem)	110	58
(9) Rayon spun with 0% stretch.	111	56^5
(10) Rayon spun with 70% stretch (two-bath process). . .	105	54
(11) Cellophane (uncoated)	128	54
(12) Cellophane (uncoated)	115	52^5
(13) Tire cord rayon-slashed(American Enka). . .	113	59
(14) Tire core rayon-slashed(American Enka). . .	116	56
(15) Lilienfeld process rayon.	108	58
(16) Cuprammonium rayon (Bemberg Corp.).	97	54
Average	111^5 ± 2^5	56 ± 0.8
(17) Fortisan rayon (Celanese Corp.)	108	49
(18) Fortisan rayon (Celanese Corp.)	108	49
(19) Mercerized ramie (reorientated)	125	47
(20) Mercerized bacterial cellulose	95	66
(21) Fiber G (du Pont)	157	46^5
(22) Fiber G (du Pont)	142	48
(23) "Amorphous" cellulose powder.	25	84
(24) Recrystallized cellulose powder	117	59
(25) Recrystallized cellulose powder	106	59
(26) Acetate rayon, saponified in 3N NH_3 at 40°C. (10 days).	98	59
(27) Recrystallized acetate rayon, saponified in 3N NH_3 at 20°C. (24 days).	114	59

continued

Specimen	I_{cr}	A_m
Spectrum Cellulose II mixed with cellulose IV		
(28) Acetate rayon, saponified in 3N NH_3 at 100°C. (6 hours)	.106	58
(29) Acetate rayon, saponified in 3N NH_3 at 100°C. (8 hours)	.109	56
(30) Acetate rayon, saponified in 0.2N NaOH at 100°C. (6 hours).	97	59
Average (26-30)	105 ± 3	58^5 ± 0.6
(31) Mercerized ramie, partially transferred into cellulose IV	.148	51
(32) Lilienfeld rayon, transferred into cellulose IV	.127	49
(33) Lilienfeld rayon, transferred into cellulose IV	.116	48^5

ide, pure cellulose II is invariably obtained, even at 100°C. It would seem that only those bases that are capable of penetrating the lattice give rise to the partial formation of cellulose IV at high saponification temperatures. (Mere heating of rayon or saponified acetates (consisting of pure cellulose II) with ammonia or sodium hydroxide of the concentrations indicated at 100°, does not give rise to cellulose IV formation.)

The figures in Table I represent sufficient evidence that the degree of crystallinity of the saponified products is constant within experimental error, independent of previous "recrystallization" of the acetate and of the saponification temperature.

In Figure 6 photometer curves are reproduced of saponification products obtained at 100°C. and at 40°C.

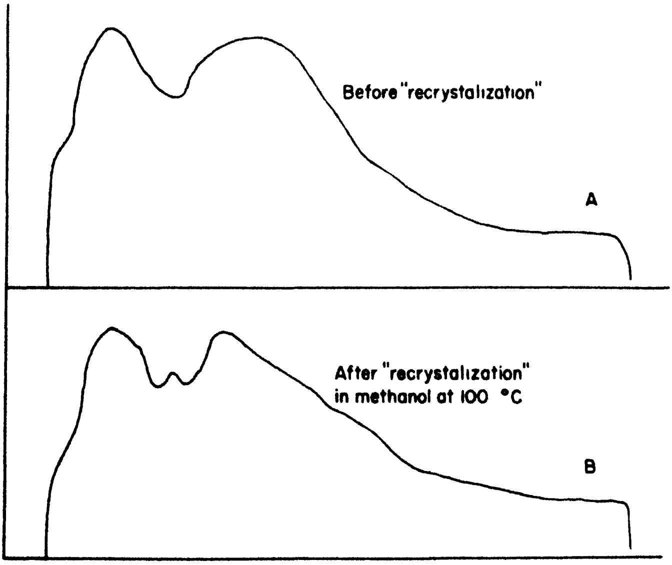

Fig. 5. Photometer curves of acetate rayon samples.

DISCUSSION

The equal degree of crystallinity of the majority of rayons (with the exception of Fiber G and perhaps Fortisan) and that of the saponified acetates is very striking and difficult to understand. It would seem, however, that this fact can no longer be denied. It will have to be accounted for in future research (5).

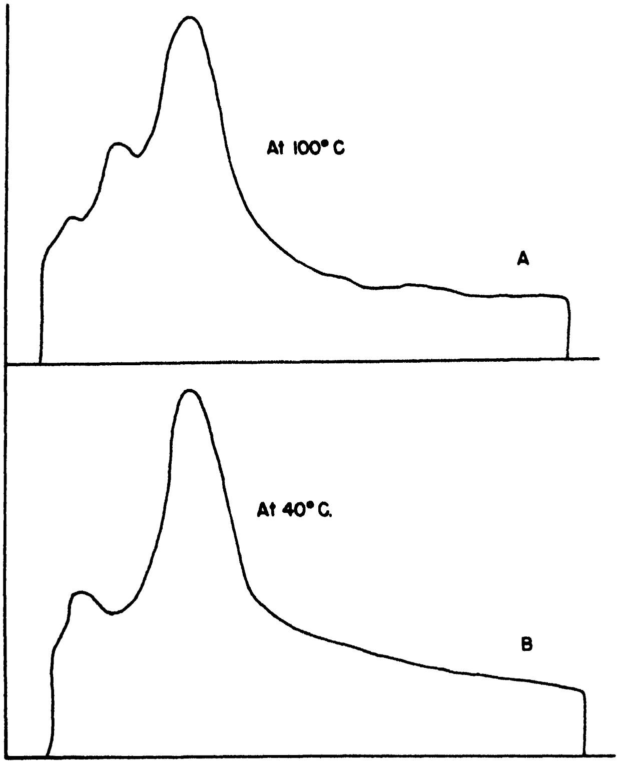

Fig. 6. Photometer curves of acetate rayon samples saponified with 3N ammonia.

The examples of wood pulp and native bacterial cellulose in the series of cellulose I, and those of Fiber G, mercerized bacterial cellulose, and the "amorphous" powder in the series of cellulose II show that the constancy found for the majority of the other representatives in these groups is neither an obligatory one, nor caused by some hidden intrinsic error in the method of evaluation. This is also corroborated by the general agreement found with the values derived from the sorption of water vapor, density, and heats of wetting (1,2,4).

Recently, numerous authors have endeavored to measure crystallinity by chemical methods. Their results show little if any conformity among each other and the figures arrived at are, as a rule, very much higher than those derived from the present x-ray experiments (6). This not surprising, since such "accessibility" measurements by means of chemical reactions will not depend merely upon the structure of the cellulose but forcibly also on the nature of the other reactants used.

It may be that the sequence of the figures found from the study of chemical reactions is the same as that of the x-ray figures; actually, in the majority of cases, such parallel sequence seems to exist roughly. What is actually measured, however, is very difficult to define.

Attention is drawn to the previously mentioned fact (1) that the ratio of the intensities of the two main peaks is nearly constant and about equal to the one theoretically predicted by Andress in the native cellulose samples investigated, whereas it is highly variable and deviates considerably from the theoretical value in the samples of regenerated cellulose. An interpretation of this phenomenon has been given elsewhere (1). It leads to the assumption of the frequent occurrence of regions with two-dimensional order rather than of three-dimensional order in regenerated celluloses.

Acknowledgment

The authors are indebted to Prof. A. J. Kluyver, Delft, and to Dr. R. D. Preston, Leeds, for samples of bacterial cellulose and Valonia. The x-ray experiments were carried out in the Physical Laboratory of the Technical University, Delft.

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5. It is recalled that O. Kratky and A. Sekora, Kolloid-Z., 108, 169 (1944), have previously shown by x-ray measurements that the degree of crystallization neither changes upon orientation nor upon drying of freshly prepared viscose filaments.
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Synopsis

The method for the evaluation of the percentage crystallinity in cellulose preparations from x-ray intensity measurements, previously described in detail (J. Appl. Phys., in press) is reviewed briefly and new material presented consisting of crystallinity percentages between 8% and 70%. Cotton, flax, and ramie possess equal crystallinity (70%) and so do the majority of rayons, independent of their degree of orientation and including cuprammonium and Lilienfeld rayons. Cellulose acetates saponified under varying conditions also yield almost the same value as rayon (40%). The new product Fiber G (du Pont) holds an exceptional position with 53% crystalline substance. In the series of native celluloses, wood pulp has about 65%, Valonia 65-70%, and bacterial cellulose about 40%. By dry grinding of rayon, a powder was obtained containing only slightly less than 10% crystalline substance, which on recrystallization in water, yields a product having the same crystallinity as rayon. The difference between the heats of wetting of the original and the recrystallized powder affords additional support of the results obtained.

Résumé

La méthode d'évaluation du pourcentage de cristallinité dans la cellulose au départ de mesures d'intensité aux rayons-x, précédemment décrite (J. Appl. Phys., in press) en détails, est brièvement rappelée; dans cette communication sont renseignés les résultats obtenus au départ de matériaux contenant un pourcentage de cristallinité de 8 à 70%. Le coton, le lin, et la ramie possèdent une égale cristallinité (70%), de même que la plupart des rayonnes, indépendamment de leur degré d'orientation, y compris les rayonnes cupriammoniques et Lilienfeld. L'acétate de cellulose, saponifiés dans des conditions variables, ont la même teneur que la rayonne (40%). Le nouveau produit Fibre G (du Pont) occupe une position exceptionnelle avec 53% de substance cristalline. Dans la série des cellulose naturelles, la pulpe de bois contient 65%, Valonia 65-70%, et la cellulose bactérique environ 40%. Par broyage de la rayonne, la poudre obtenue contient seulement un peu moins de 10% de substance cristalline; par recristallisation dans l'eau cette poudre fournit un produit possédant le même taux de cristallinité que la rayonne. La différence entre les chaleurs de mouillage de la poudre initiale et de la poudre cristallisée confirme en outre les résultats obtenus.

Zusammenfassung

Es wird die Methode fuer die Berechnung der prozentuellen Kristallinitaet in Cellulose-Praeparaten aus Roentgen-Intensitaetsmessungen, die frueher in Einzelheiten (J. Applied Phys., in Druck) beschrieben wurden, kurz wiedergegeben und neues Material für Kristallinitaets-Prozente zwischen 8% und 70% mitgeteilt. Baumwolle, Flachs, und Ramie besitzen die gleiche Kristallinitaet (70%), dasselbe gibt für die Mehrzahl der Kunstseiden (unabhaengig vom Grad der Orientierung und einschliesslich der Cupra-Ammonium- und Lilienfeld-Seiden). Celluloseazetate, die unter verschiedenen Bedingungen verseift waren, geben denselben Wert wie Kunstseide (40%). Neue Fiber G (du Pont) zeigt ein Ausnahmeverhalten mit 53% kristalliner Substanz. Unter den natuerlichen Celluloseprodukten zeigt Zellstoff 65%, Valonia 65-70%, und Cellulose von Bakterienursprung ungefaehr 40%. Durch Trockenmahlung von Kunstseide wird ein Pulver hergestellt, das weniger als 10% kristalline Substanz enthaelt und das bei Rekristallisation in Wasser eine Substanz gibt, die dieselbe Kristallinitaet wie Kunstseide hat. Diese Resultate werden unterstuetzt durch die Werte fuer den Unterschied zwischen der Benetzungswaerme der urspruenglichen und rekristallisierten Pulver.

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Degree of Lateral Order in Various Rayons as Deduced from X-Ray Measurements*

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INTRODUCTION

In the preceding publication (1) it was shown that little if any variations in over-all crystallinity are found in the majority of rayon specimens, the sole obvious exception being Fiber G (du Pont). This conclusion is based on the constancy of the total intensity diffracted by the "crystalline" portion (integrated surface of peaks). Investigations were carried out, therefore, to determine whether other differences in the x-ray pictures could be detected. To that end the integrated intensities of the two principal peaks and their half-widths were measured separately.

EXPERIMENTS

The technique applied in our exposures leads to a rather significant artificial broadening of the single lines, owing to the use of a relatively large pinhole (0.8 mm.), and objects of 1.6-mm. thickness. Consequently, interference lines lying near to each other merge into one single peak on the photometer curves.

The reflections which consist of the two main peaks exhibited by the photometer curves are given in Table I. The theoretical intensities according to Andress' data are also listed.

TABLE I. Survey of Reflections Contributing to the Two Main Peaks.

	Reflections		Theoretical intensities		Ratio II/I
Specimens	Peak I	Peak II	Peak I	Peak II	
Cellulose I	101 + $10\bar{1}$	021 + 002	140	442	3.15
Cellulose II	101	021 + $10\bar{1}$ + 002	75	477	7.35

The intensity ratio, peak II/peak I, actually found (hereafter simply designated as "ratio"), is given in the first column of Table II. Also given are the measured half-width values of both peaks (in millimeters) on the photometer curves (which were taken with a linear magnification of 3.9), distance of sample to film, 40 mm. Since we are interested only in the relative values, these figures will serve the purpose. (The accuracy of these figures is not very great—the error is estimated to be ±0.5 mm.).

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*Contribution No. 55 from the Laboratory for Cellulose Research, Utrecht.

It is seen that in the native celluloses the ratio does not show much fluctuation and remains below, though not very far from, the figure that follows from Andress' theoretical evaluation of the lattice.

TABLE II. Intensity Ratios and Half-Width Values of the Two Peaks Measured on the Photometer Curves (Linear Magnification x 3.9).

Specimen	Ratio, II/I	Half-width values, mm.	
		I	II
(1) Standard cotton	2.10	12	8^5
(2) Ramie (purified and bleached)	1.9	13	9^5
(3) Ramie (purified and bleached)	2.4	13^5	10^5
(4) Cottonine (flax)	2.1	12^5	10
(5) Cotton linters (mfgd. for viscose process)	2.2	11	10
(6) Sulfite wood pulp from spruce	2.06	12^7	10^4
(6a) Valonia cell wall (*Valonia ventricosa*)	1.78	14	7^5
(7) Bacterial cellulose (*Bacterium xylinum*)	2.6^5	13	10^5
Spectrum Cellulose II			
(8) Viscose staple fiber (AKU=Arnhem)	10	9^5	13
(9) Rayon spun with 0% stretch	13.7	8	13^5
(10) Rayon spun with 70% stretch	13.8	6^5	13^5
(11) Cellophane (uncoated)	12.2	8	12^5
(12) Cellophane (uncoated)	14.3	8^5	12^5
(13) Tire cord rayon-slashed (American Enka)	-	-	-
(14) Tire cord rayon-slashed (American Enka)	15.6	6^5	15^5
(15) Lilienfeld process rayon	11.4	9^5	14
(16) Cuprammonium rayon (Bemberg Corp.)	9.7	8	12
(17) Fortisan rayon (Celanese Corp.)	15.0	6	12^5
(18) Fortisan rayon (Celanese Corp.)	15.0	7	12^5
(19) Mercerized ramie (reorientated)	17	6^5	12
(20) Mercerized bacterial cellulose	13.5	8	12
(21) Fiber G (du Pont)	15.6	6^3	11^3
(22) Fiber G (du Pont)	17.7	5	11^5
(23) "Amorphous" cellulose powder	-	-	16^5
(24) Recrystallized cellulose powder	14.8	7	14
(25) Recrystallized cellulose powder	11.8	9	14^5
(26) Acetate rayon, saponified in 3N NH_3 at 20°C. (24 days)	14.4	7^5	14
(26a) Acetate rayon, saponified in 3N NH_3 at 40°C. (10 days)	11.9	8	13^5
(27) Recrystallized acetate rayon, saponified in 3 N NH_3 at 20°C. (24 days)	29.0	5	14

The half-width values do not exhibit significant variations, perhaps with the exceptions of peak II in cotton and Valonia, which are obviously narrower than in the other fibers.

On the contrary, in the specimens that exhibit the spectrum of cellulose II, the ratio is always higher than the theoretical value and is, moreover, very variable; so is the half-width of peak I, which consists merely of the 101 lines in this case (see Table I). Peak II shows much less variation. Its half-width is between 12 and 13^5 in the majority of cases; in specimen numbers 14 and 15 it is somewhat broader; in Fiber G (21-22) slightly sharper. The integrated intensity of peak II (not listed) was also constant within about 10%. The variations in the intensity ratios, therefore, are parallel with the variations in half-widths of peak I. Figure 1 demonstrates the obvious correlation between the two figures.

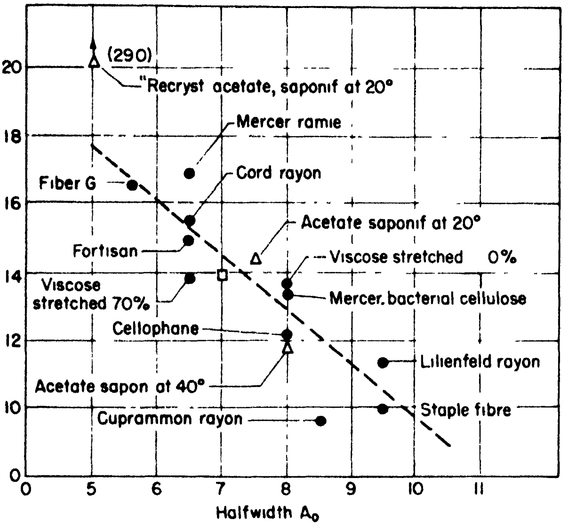

Fig. 1. Intensity ratio, peak II/peak I, in samples containing cellulose II plotted against the half-width of peak I.

DISCUSSION

The question arises as to how these observations can be interpreted. The answer may be as follows. In the native specimen investigated, where the intensity ratios and the line breadth exhibit little variations, the crystallites seem to possess almost the same average size, shape, and degree of perfection. The average number of well-ordered molecular layers in various directions does not vary appreciably from specimen to specimen. In the regenerated fibers, on the contrary, the shape and perfection of the crystallites vary considerably. Kratky has conclusively proved by experiments on low-angle scattering that the crystallites in rayon are lamelliform. They are ribbon-shaped (see Fig. 2) and the 101 plane (A_0) is in the plane of the ribbon whereas the $10\bar{1}$ and 002 planes (A_3 and A_4) lie at large angles to the ribbon plane. For simplicity of description we may substitute the $10\bar{1}$ and 002 planes by one single plane corresponding to the A_3-A_4 doublet (A_3 in Fig. 2) perpendicular to the plane of the ribbon. In all rayons, the intensity ratio is larger than the theoretical one. This means that order according to the A_3 plane is favored over the order according to the A_0 plane; this is only another way of expressing that the crystallites are preferentially lamelliform, owing to the fact that the cohesive forces between the A_3 planes are very much stronger than those between the

A_0 planes. The differentiation between one specimen and another is the degree in which A_0 order is inferior to the A_3 order.

In Figure 2 the transitional area (fringe area) between a crystalline and an amorphous region is also schematized. Cleavage according to A_0 is favored over cleavage according to A_3. One can even imagine the existence of many spots where there may be merely order in A_3 and none in A_0 (two-dimensional lateral order). Such spots will contribute to the intensity of the second peak and not to that of the first peak.

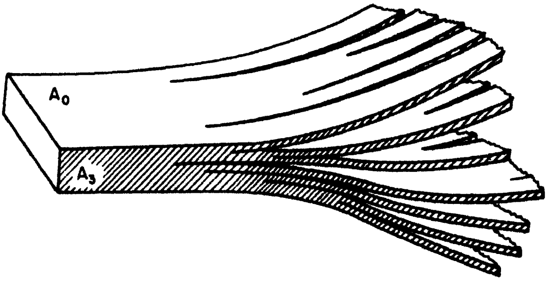

Fig. 2. Diagram of a part of a crystallite and a fringelike transitional area.

The differences between the various rayons are differences in the distribution of lateral order in one particular direction perpendicular to that of the molecular chains, i.e., the direction perpendicular to the A_0 plane. Order in the other lateral direction (A_3) is nearly constant in all specimens.

The x-ray results show that if the average thickness and perfection of the lamellae increase (line 101 sharper), the total number of well-ordered 101 plane contracts diminishes (integrated intensity drops). The total mass of lattice-ordered substance thereby remains constant. In other words, thicker and better formed lamellae involve a smaller number of ordered A_0 plane contacts.

This picture is not inconsistent with current views regarding the structure of cellulose gels as representing networks of rather stiff chains. Since A_0 planes are those planes whose cohesion in the lattice is weakest, they will always tend to be the most poorly ordered ones. The A_3 contacts are the preferred ones and their number is almost constant. (The intensity ratio, peak II/peak I, is always larger than the theoretical one.)

If, by some process of "recrystallization," lamellar order improves in certain nuclei, tensions will arise in the immediate vicinity of the nuclei and other lamellae (possibly smaller or imperfect) are torn loose en revanche. Order with respect to the A_3 plane, held together by much stronger cohesive forces, is not, or is much less, affected.

A nice support of this explanation seems to be afforded by the saponified acetate rayons listed in Table II. The two saponified rayons obtained by low-temperature saponification of ordinary acetate rayon take an average position in Figure 1 (triangles). The fiber obtained by low-temperature saponification of a previously "recrystallized" sample of acetate rayon, on the other hand, takes a very extreme position (triangle in top left part of the figure), although its total crystallinity is no different. Its 101 line is unusually sharp and it also has a very low total intensity amounting to no more than 3-4% of that of the second peak. It would seem that the "recrystallization" of the acetate, as provoked by previous heating in methanol, involves a similar process of redistribution of the total amount of lattice ordered substance.

Provided the process of recrystallization is interpreted strictly in that way, we may perhaps still, in a sense, associate various degrees of recrystallization with the various rayon specimens investigated. It then appears that the highly orientated rayons (where some kind of improved order is most readily expected) actually lie in the upper left part of Figure 1 (except Lilienfeld rayon, which seems to represent a particular case).

In may be that in measurements of accessibility by means of chemical reactions (see the preceding paper (1)) the states of lateral order referred to above play a certain part, which, in part at least, may also account for the entirely different results obtained by such methods as compared with the total crystallinity figures deduced from x-ray work.

In chemical reactions, with conservation of the fiber form, x-ray work shows that it is always the 101 plane that is affected first. The location of the 101 line, its sharpness, or its intensity, is then affected, often long before any change in the 002 or other lines is observed. The same applies to many cases of intramicellar swelling of cellulose and its derivatives. This is entirely consistent with the view developed here.

Acknowledgment

The author wishes to acknowledge the cooperation of Dr. A. Weidinger who carried out the x-ray work in the Physical Laboratory of the Technical University at Delft.

REFERENCE

1. See also contribution No. 54 from the Laboratory for Cellulose Research (this issue, page 135).

Synopsis

X-ray measurements on 16 different specimens of regenerated cellulose reveals that there exists a pronounced negative correlation between the integrated intensity of the 101 interference and its halfwidth. The 101 plane is a preferred cleavage plane and represents the lamellar plane of the ribbon-shaped crystallites. Variations in the intensity of the other interferences are much less or nonexistent. These results show that the degree and the perfection of lateral order according to the $10\bar{1}$ and 002 planes is little at variance, but that order according to the 101 plane is extremely variable in such a way that if the average thickness and (or) perfection of the lamellae increases, the total number of well-ordered 101 plane contacts diminishes. As a possible explanation of this phenomenon it is suggested that various degrees of recrystallization with reference to this

particular plane (i.e., various degrees of lateral order) may be associated with the various rayon specimens. This, however, does not necessarily imply differences in the total amount of ordered substance. This explanation is corroborated by the fact that cellulose acetate fibers which were previously allowed to "recrystallize" by heating in methanol, after saponification yield a rayon with a particularly sharp, but also particularly weak, 101 interference, without exhibiting a higher total percentage of ordered substance than the saponification products of acetate treated in this manner.

Résumé

Les mesures, effectuées aux rayons X sur seize échantillons différents de cellulose régénérée, prouvent qu'il existe une corrélation négative prononcée entre l'intensité intégrée de l'interférence 101 et sa demi-largeur. Le plan 101 est un plan de clivage préférentiel, et constitue un plan lamellaire des cristallites striés. Les variations d'intensité des autres interférences sont moindres ou inexistantes. Ces résultats semblent montrer que le dégre et la perfection d'ordre latéral par rapport aux plans $10\bar{1}$ et 002 sont en faible désaccord; par contre, l'ordre par rapport au plan 101 est extrèmement variable, de telle façon que si l'épaisseur moyenne ou la perfection des lamelles s'accroît, le nombre total de plans 101 adéquatement disposés s'accroît. Une explication possible de ce phénomène consiste en ce que des dégres variables de recristallisation par rapport à ce plan particulier (degrés différents d'ordre secondaire) peuvent être associés aux différents échantillons de rayonne. Ceci, toutefois, n'implique pas necéssairement des différences dans la quantité totale de substance ordonnée. Cette explication est confirmée par le fait que les fibres d'acétate de cellulose, auxquelles une recristallisation a été rendue possible par chauffage dans le méthanol, fournissent après saponification, une rayonne, caractérisée par une interférence bien nette, mais remarquablement faible 101, sans manifester un pourcentage total en substance ordonnée plus élevé que les produits de saponification d'acétates, qui n'ont pas subi le même traitement.

Zusammenfassung

Roentgenstrahlenmessungen an 16 verschiedenen Proben regenerierter Cellulose zeigen, dass eine ausgeprägte negative Korrelation zwischen den integrierten Intensitäten der 101 Interferenzen und ihrer Halb-breite existiert. Die 101 Ebene ist eine herorzugte Spaltebene und entspricht der lamellaren Ebene der bandformigen Krystallite. Die Abweichungen in den Intensitäten der anderen Interferenzen sind viel kleiner oder kommen nicht vor. Diese Ergebnisse deuten an, dass der Grad und die Vollkommenheit der seitwärtigen Anordnung nach den 101 und 002 Ebenen wenig abweichen, dass aber die Anordnung nach den 101 Ebenen in der Weise Schwankungen unterworfen ist, dass wenn die durchschnittliche Dicke oder Vollkommenheit der Lamellen steigt, die Anzahl gutgeordneter Berünhrungspunkte der 101 Ebenen abnimmt. Zur Erklärung dieses Phänomens wird vorgeschlagen, dass verschiedene Grade der Neukrystallisierung mit Bezug auf diese besondere Ebene (d.h. ver-

schiedene Grade seitwärtiger Proben) in den verschiedenen Kunstseide Exemplaren vorkommen. Das hat nicht zwangsweise Verschiedenheiten in dem Inhalt geordneter Substanz zur Folge. Diese Erklärung wird dadurch unterstützt, dass Celluloseazetatfasern die zuerst durch Erhitzen in Methylalkohol auskrystallisiert wurden, nach Verseifung eine Kunstseide liefern mit besonders scharfer, aber auch besonders schwacher 101 Interferenz, ohne dass der Prozentsatz geordneter Masse höher ist als in Verseifungprodukten von Azetat des nicht so behandelt wurde.

Received June 25, 1948

REVIEW

THE TECHNOLOGY OF ADHESIVES. John Delmonte. Reinhold, New York, 1947. 516 pp. Price $8.00.

A comprehensive source book on adhesives has long been desirable, and the need has been largely obviated by the bringing together of a miscellany of scattered information of an empirical nature by Delmonte. Included are exhaustive compilations of data on phenolic, urea and melamine, and vinyl-type resins useful as adhesives. Natural polymeric substances as source materials for adhesives are discussed under headings on cellulose, proteins, dextrin, and shellac. As an alternate approach, several chapters are devoted to adhesives for specific purposes, as for wood, plastics, metal, rubber, paper, and mica. A final chapter is concerned with the testing of adhesives.

At present, any treatise in this field clearly reveals the paucity of experiments designed to increase our understanding of adhesion. The author has a well-thought-out chapter on the theories of adhesive action. Recently a number of such reviews have appeared—by Weyl, Hofrichter, de Bruyne, and others. All reviews serve to show that except for the early work of McBain little advancement has been made in the science of adhesion. Merely quoting equations of Gibbs and of Langmuir and data on monolayers on liquids does not appreciably further our knowledge concerning the adhesion properties of the many resins extensively described by Delmonte. What is needed in the field of the adhesion of high polymers is a new approach and more research, now that new and exciting tools are at hand. This is the reviewer's feeling after going over this excellent contribution to the literature on adhesives.

The book contains voluminous literature references at the end of chapters and an excellent index. It is a book that practicing polymer and adhesive chemists will want to own.

A. F. Chapman

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Simple Presentation of Network Theory of Rubber, with a Discussion of Other Theories

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It seems now to be generally agreed that soft rubberlike materials consist of long flexible molecules more or less completely linked into a coherent network by chemical bonds formed during cure. These bonds suppress, for the most part, the plasticity that the liquidlike mass of molecules would otherwise have, but leave the molecules free to take on a great many configurations of essentially the same energy under the influence of thermal agitation. The tendency of stretched rubber to retract is then understood as a kinetic phenomenon, like the tendency of a gas to expand: it is the tendency of a system to assume the form of maximum entropy when the internal energy is essentially independent to form.

There is no similar agreement as to what constitutes an adequate theoretical treatment of such materials. In particular, there exists a wide variety of formalisms for the derivation of the stress-strain relation of an ideal soft rubber. These are usually referred to as network theories, though the only treatment that actually deals with a general network of flexible molecular chains is that of the authors (1). Other treatments have been based on the consideration of individual elements or small groups of elements from networks, concerning the behavior of which special assumptions were made, or they have proceeded on the basis of general ideas that involve no reference whatever to the network structure of the material. The relation of these theories to the general network theory of rubber is the subject of the present paper.

As background for the discussion of other theories we shall first develop the theory of rubber, considered as a random network of long flexible molecules, in a particularly simple way.* The ease

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*The treatment given here starts from the same basis as that of reference 1, but proceeds in a simpler way to a more restricted result—the derivation of the stress-strain relation. This analysis concentrates attention on the entropy, as in the custom of other writers on the subject; our earlier one shifted attention at the earliest possible moment from the entropy to the average forces exerted by the network segments, since this seemed to give a better picture of the detailed relations between network elements. The significance of our earlier analysis of the general rubber network has been widely overlooked, partly because its detailed character led to its being put in an Appendix, and partly because of its unconventional approach to the with which a network of general form can be treated will make it evident that there is little need to base network theories of rubber on the use of more special models. Next, we shall examine an idea that appears in many discussions of rubber which employ simplified models—the idea that the junctions of the rubber network can be treated as if they were fixed in space. We shall show that this picture of the situation is quite unrealistic: the junctions have a Brownian motion comparable to that of any portion of the intervening molecular segments. The common assumption to the contrary does not affect the results of some types of calculations, but it is inadmissible in the treatment of other problems. Finally, we shall show that the theory of Wall (2), which employs no special model, is based on postulates that are inconsistent with the network structure of rubber.

I. ELEMENTARY PRESENTATION OF NETWORK THEORY OF RUBBER

We start the formulation of our picture of rubber by the consideration of milled rubber. All rubbers—natural or synthetic—are composed of very long flexible molecules. When raw rubber is milled, such structure as formerly existed in it is broken down, and the milled rubber becomes essentially a liquidlike mass of flexible rubber molecules. This mass is highly viscous, because the tendency of the long flexible molecules to become tangled with each other impedes their relative motion, but, as with any liquid, there is no definite form to which it will return when external forces are removed.

The process of cure introduces into this mass the elements of structure which hold the molecules in fixed relations to each other and suppress the plasticity. It consists in the introduction of strong and definite bonds between the long molecules which eventually link them into a coherent network extending throughout the whole mass; it is the definite structure of this network that determines the definite form of the material under zero external force. This network will be highly irregular, being formed by the introduction of bonds essentially at random, but on the average it will be homogeneous and isotropic when the material is unstretched. Not all of the rubber molecules will be actively involved in it. There will be many side chains and loose ends, as well as material not bound into the network, part of it extractable by solvents, part consisting of snarls inextricably entangled with the network.

In lightly cured materials there will be relatively few of these bonds introduced. On the average, each molecule will be involved in only a few bonds; a relatively small portion of each molecule will be involved in the formation of intermolecular bonds. Only near these bonds will the molecules be brought into definite relations to their

subject. In particular, we must call attention again to the fact that the simple three-dimensional network employed for purposes of visualization in the body of reference 1 was introduced only after it was proved to be equivalent for the purposes at hand to a network of arbitrary form. This equivalence also follows easily from the treatment in Section I of the present paper.

neighbors. Over most of their great length the molecules will exert the same forces on, and be in the same relation to, adjacent molecules as in the liquidlike milled rubber. In particular, the Brownian motion of the molecules will not be suppressed. They will move past each other and take on a great variety of configurations, just as they would if immersed in a foreign liquid–the only restraints on their Brownian motion being those impressed by the relatively few fixed bonds between the molecules.

We shall consider a soft rubberlike substance, then, as a liquidlike mass of flexible molecules subject to the permanent constraints implied by their union into a coherent network by bonds formed at relatively few points. It is the presence of these bonds–which tend to control the form of the material–that differentiates rubberlike materials from liquids. It is the small number of these bonds–and their weak control of the form of the material through the entropy rather than through the internal energy–that differentiates rubberlike materials from ordinary solids.

We shall discuss the behavior of rubber by consideration of two thermodynamic functions: the internal energy U and the entropy S. From these, one can determine the force Z tending to change a dimension L of the system, as:

$$Z(L,T) = (\partial U/\partial L)_T - T(\partial S/\partial L)_T \tag{1}$$

where the derivatives are to be taken with the perpendicular dimensions constant (cf. equations 18 and 19).

Aside from a constant contribution due to the formation of intermolecular bonds, the internal energy of a soft, uncrystallized, unstretched rubber is the same as that of a liquid of rubber molecules. We shall assume that the internal energy of rubber, like that of any liquid, will not depend at all on the form of the material, but only on its volume and temperature. In doing so, we shall neglect the change in potential energy of the molecules when they are bent or extended, up to the point where they are completely straightened out and further extension will involve stretching of valence bonds in the molecule; in other words, we treat the molecules as being perfectly flexible. We also neglect changes in the internal energy due to the increasing alignment of the molecules as the material is stretched. This is permissible only as a first approximation, and for not too great extensions of the material.* We write, then, as for a liquid:

$$U = U(V,T) \tag{2}$$

U has a sharp minimum with respect to variation of V at the normal volume of the material; the volume of the material under given external forces is largely determined by U. The exact form of the function U (V,T) will depend on the forces with which the molecules interact, and will thus depend, for instance, on the number and character of the side chains and polar structures which may be present in the molecules. Such features of the structure, which vary from one rubberlike material to the next, will in effect determine the compressibility and the coefficient of thermal expansion for the material. For this treatment of rubberlike elasticity it is not necessary to consider these intermolecular forces in detail; they enter only through the compressibility and coefficient of thermal expansion, which appear in the theory as observable constants.

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*It is to be emphasized that the internal energy depends strongly on the form of the material when crystallization takes place, as when the material is subject to large extension. We shall not consider such cases here.

As with gases and liquids, the entropy of such a system of flexible chains has, in statistical terms, a relatively simple form. It is characteristic of these systems that there are accessible to the components an enormous number of configurations, all with essentially the same low potential energy. Configurations of higher potential energy are also possible, as when molecular chains are stretched or the separations of atoms are otherwise changed, but these occur with relatively small probability. Under these circumstances the entropy can be expressed, with sufficiently good approximation, as the sum of two parts. The first, S_1, associated with the kinetic energy of the network or the thermal capacity of the material, is primarily a function of the temperature, but may depend slightly on the volume. The second is related to the number, C, of low energy configurations accessible to the system:

$$S_2 = k \ln C \tag{3}$$

The number of configurations accessible to the network will depend upon the external form of the material; C, and thus S_2, will be a function of the form of the material, but will be independent of its temperature. For a rectangular parallelepiped of rubber, with edges of lengths L_x, L_y, L_z:

$$S = S_1(V,T) + k \ln C(L_x, L_y, L_z) \tag{4}$$

The first of these terms will need no detailed discussion here.

In enumerating the configurations possible for a network, and evaluating the second term in the entropy, some simplification of the physical picture is unavoidable. Any simplified model must, however, give an adequate representation of the following features of the real system: (1) the flexibility of the molecules, which makes it possible for each constituent segment of the network to take on a great number of configurations; (2) the constraints implied by the union of the chains into a network, which make it impossible for the chains to take on all configurations independently; and (3) the volume-filling property of the molecular chains, which prevents any two of them from occupying the same region in space simultaneously.

In the mathematical treatment of the system, the flexibility of the molecules enters through the functions that give the number of configurations possible for each individual section of chain when its ends are fixed at various separations. These functions we shall call the configuration functions for the chain segments. Now, whatever the structure of a flexible chain, its configuration function may be taken as of Gaussian form:

$$c(r) = C_1 e^{-C_2 r^2} \tag{5}$$

r being the separation of the ends, under just two conditions: (1) the chain must be long as compared to any part of it with appreciable stiff-ness, and (2) only separations of the ends which are sufficiently small compared to the total length of the chain shall be considered (3). In the present discussion we shall restrict our attention to lightly cured materials in which all chain segments between junctions in the network are long, and shall consider only moderate extensions of the material, such that the segments are, on the average, not highly extended. Accordingly, without regard for any special characteristics of the molecular chains, we can assume with good approximation that every segment of the network has a configuration function of Gaussian form.

The constant C_2 in the configuration function will vary with character and length of the chain. It is often convenient to characterize each chain not by the constant C_2, but by a parameter N defined by:

$$C_2 = \frac{3}{2Nl^2} \tag{6}$$

writing:

$$c(r) = C_1 \exp\{-\frac{3}{2Nl^2} r^2\} \tag{7}$$

This expression is of the form of the configuration function, for small extensions, of a chain of N independent links of fixed length l (3a). Without in any way restricting the generality of our discussion, we can apply the same formalism in dealing with other types of flexible chain, such as occur in actual rubbers. The length l is a parameter characteristic of a material and N may vary from segment to segment.

In calculating the number of configurations possible for the molecular chains in a piece of rubber, the essential constraints are those implied by the linking of these chains into a network. Of these we shall take full account.

In addition, there are the constraints, which we shall term steric hindrances, that arise from the fact that two molecules cannot occupy the same volume in space or pass through each other. This volume-filling property of the molecules makes itself felt in its control of the volume of the material, largely through the internal energy. It also affects the entropy by eliminating from consideration all configurations of the network in which two portions of a chain occupy the same volume. These steric hindrances would have a complicated effect in a detailed enumeration of the configurations possible for the network, and it is necessary to neglect them. Justification of this approximation is an important step in the development of the theory of rubberlike materials. The argument required is given in Appendix A to avoid undue interruption of the main argument at this point. Fortunately, the result of the discussion is simple: in lightly cured materials, not overly stretched, the steric hindrances change the number of configurations possible for the network by a constant factor. This factor, independent of the form of the material, does not affect the forces exerted by the material, and can be neglected here.

To summarize, in computing the entropy of rubber we shall consider it as an arbitrary network of chains with Gaussian configuration functions, subject to all the constraints implied by their union into a coherent network, but free from other constraints. Such a network we shall call a Gaussian network.

We now define certain terms needed for the precise statement of our methods and results. These are illustrated in Figure 1.

By the "fixed points" of the network we mean the points at which it is immobilized by external constraints. It is at these points that the network exerts forces on the external system, and, conversely, that the external system exerts forces on the network. The positions of the fixed points will determine the external form of the material.

By the active portion of the network we mean that portion of the network that stretches between the fixed points and contributes to the forces exerted by the network on these points. A portion of chain is part of the active network if and only if it is part of some non-retracing path along the chains from one fixed point to another. The rest of the material may be described as unattached material and loose ends, the latter category including perhaps quite complicated chain structures attached to the network at a single point.

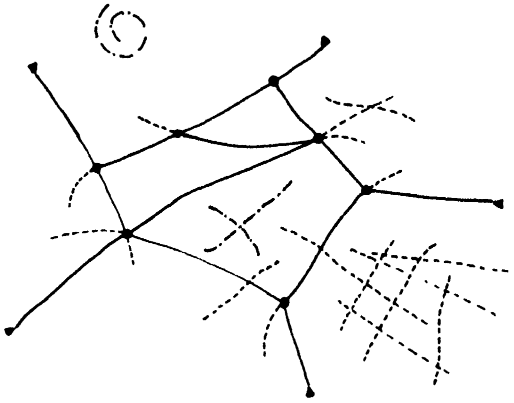

Fig. 1. Terminology for description of network. The segments are to be considered as bonded together wherever they cross. Segments of active network (solid line); loose ends (broken line); unattached material (-•-•); fixed points (▲); junctions of active network (●).

The term "junction" typically includes all points of bonding between molecules; a "segment" of the network is a portion of a molecular chain that extends between two adjacent junctions of the network. In considering the active network alone, we shall consider as junctions only the points of union of segments of the active network; we exclude from consideration, for instance, the points at which loose ends are bonded to a segment of the active network.

Now the essential characteristic of the active part of the network, as we have defined it, is that it contributes to the entropy a term that depends upon the positions of the fixed points, that is, upon the external form of the material. In the case of a system of independent flexible chains, the number of configurations possible for the system as a whole is the product of the number of configurations possible for each of the independent parts. The entropy, essentially the logarithm of this number, will be, correspondingly, a sum of contributions from the independent molecules, and will be independent of the form of the material unless each molecule is somehow subjected to a constraint depending on the form of the material. In the case of a network structure, the number of configurations possible for each of the loose ends and for each portion of unattached material will be independent of the positions of the fixed points. The number of configurations possible for the system as a whole will involve as factors each of these numbers, together with the number of configurations possible for the active network, which does depend on the position of the fixed points. The entropy, correspondingly, is the sum of contributions from the loose ends and the unattached material, which will be independent of the form of the material, and a contribution from the active network, which will depend on the form. As is evident from equation 1, it is only the latter part of the entropy that will contribute to the forces exerted by the system against external constraints. In computing such forces it is thus possible to consider the network as stripped down to its active part.

The number of configurations possible is easily computed for an arbitrary active network. First of all, one can immediately write the number of configurations consistent with any given set of positions of the fixed points and junctions of the network. Let the positions of these points be indicated by Cartesian coordinates (x_τ , y_τ , z_τ ,) or the vector r_τ . When it is necessary to distinguish junctions from fixed points we shall use numerical or letter subscripts for the former, and subscripts α , β ,...for the latter. Let the chain segment joining the points (x_τ , y_τ , z_τ) and (x_ν , y_ν , z_ν) be one of $N_{\tau\nu}$ links, with configuration function:

$$c(|r_\tau - r_\nu|) = C_{\tau\nu} \exp\{-\frac{3}{2N_{\tau\nu} l^2}[(x_\tau - x_\nu)^2 + (y_\tau - y_\nu)^2 + (z_\tau - z_\nu)^2]\} \tag{8}$$

Given the positions of the junctions and fixed points, the chain segments are otherwise independent, in the present approximation of neglected steric hindrances. The number of configurations possible for the network is then simply the product of the number of configurations possible for the individual segments:

$$C(r_\alpha, r_\beta, \ldots r_1, r_2, \ldots) = C_0 \exp\{-\frac{3}{2l^2}\sum_\tau \sum_\nu \frac{1}{N_{\tau\nu}}[(x_\tau - x_\nu)^2 + (y_\tau - y_\nu)^2 + (z_\tau - z_\nu)^2]\} \tag{9}$$

the sum being over all pairs of points (fixed points or junctions) that are connected by chain segments.

To determine the total number of configurations of the network consistent with given positions of the fixed points only, we now have to sum $C(r_\alpha, r_\beta \ldots r_1, r_2 \ldots)$ over all possible sets of positions of the junctions. In the approximation in which all configuration functions are of Gaussian form, each junction can take on any position in space, whatever the positions of other junctions.* The total number of configurations as a function of the positions of the fixed points is then:

$$\mathfrak{C}(r_\alpha, r_\beta, \cdots) = \int dx_1 \int dy_1 \int dz_1 \int dx_2 \int dy_2 \int dz_2 \cdots C(r_\alpha, r_\beta, \cdots r_1, r_2, \cdots) \tag{10}$$

the integrations being over the coordinates of all network junctions.

Complete evaluation of this integral is possible (4) but not necessary for the purposes of this argument. We note that the integral can be expressed as the product of three factors involving, respectively, the x, y, and z coordinates. The x factor is:

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*In the actual network the separation of adjacent junctions is limited by the length of the chain segment connecting them. With the equivalent Gaussian network, greater separations are possible, but the "configurations" possible for these separations are so few that it makes no difference whether we count them or not.

$$\int dx_1 \int dx_2 \int dx_3 \cdots \exp\{-\frac{3}{2l^2} \sum_{\tau>\nu}\sum \frac{1}{N_{\tau\nu}} (x_\tau - x_\nu)^2\}$$

The effect of the integrations on the form of the integrand is easily ascertained. If we single out the coordinate x_1 for special attention, we can rewrite the integrand, completing the square of the terms in x_1 in the exponent in the familiar way, to obtain:

$$\exp\{-\frac{3}{2l^2}(\sum_\tau \frac{1}{N_{1\tau}})[x_1 - L(x_\alpha, \cdots x_2, \cdots)]^2 - \frac{3}{2l^2} Q(x_\alpha, \cdots x_2, \cdots)\}$$

where L is a linear form and Q a quadratic form in all x's but x_1. Integration over x_1 affects only the first factor, replacing it by a constant multiplier; the multiple integral becomes:

$$k_1 \int dx_2 \int dx_3 \cdots \exp\{-\frac{3}{2l^2} Q(x_\alpha, \cdots x_2, x_3, \cdots)\}$$

Similarly, integration over x_2, x_3,... eliminates the variable in question from the integrand, but leaves this as an exponential of a quadratic form in the remaining variables. After integration over the coordinates of all junctions there then remains an exponential of a quadratic form in the coordinates of the fixed points only, which can be written as:

$$C_0 \exp\{-\frac{3}{2l^2} \sum_{\alpha>\beta}\sum \frac{1}{N'_{\alpha\beta}} (x_\alpha - x_\beta)^2\}$$

the sum being over all pairs of fixed points. The $N'_{\alpha\beta}$ are constants, having the character of the number of links in a chain, which in general may depend on all the constants $N_{\tau\nu}$ (8). The y and z integrals are of exactly the same form, and the results of the integrations are the same, x being replaced by y or z throughout. Thus it is evident that:

$$\Phi(r_\alpha, r_\beta, \ldots) = C_1 \exp\{-\frac{3}{2l^2} \sum_{\alpha>\beta}\sum \frac{1}{N'_{\alpha\beta}} [(x_\alpha - x_\beta)^2 + (y_\alpha - y_\beta)^2 + (z_\alpha - z_\beta)^2]\} \qquad (11)$$

The form of this result is independent of the character of the network, which makes itself felt only through the constants C_1 and $N'_{\alpha\beta}$. It will be noted that this expression is the same as that which would be found if the network consisted simply of independent chains of $N'_{\alpha\beta}$ links running between the fixed points α and β. As concerns entropy and entropy forces, then, an arbitrary Gaussian network can be replaced by a corresponding set of independent Gaussian chains running between each pair of fixed points. This simplified equivalent network is conveniently employed in certain types of computation.

The special case to which we shall now devote our attention is that of a piece of rubber which at a standard temperature and in the absence of external forces is a unit cube, but which is subjected to uniform stretching parallel to the edges until these have lengths L_x, L_y, L_z. If all external forces are applied normal to the surfaces, the fixed points will lie on these surfaces in positions which change in proportion to the corresponding dimensions of the material. If three of the faces of the parallelepiped are taken as the coordinate planes:

$$x_\alpha = x_\alpha^{(o)} L_x \qquad y_\alpha = y_\alpha^{(o)} L_y \qquad z_\alpha = z_\alpha^{(o)} L_z \tag{12}$$

$x_\alpha^{(o)}$, $y_\alpha^{(o)}$, $z_\alpha^{(o)}$ being the coordinates of the α^{th} fixed point when the material is unstretched and at the standard temperature.* The number of configurations possible for the network, now a function of L_x, L_y, L_z, then becomes simply:

$$\mathfrak{C}(L_x, L_y, L_z) = K_1 \exp\{-(K_x L_x^2 + K_y L_y^2 + K_z L_z^2)\} \tag{13}$$

where:

$$K_x = \frac{3}{2l^2} \sum_{\alpha>\beta}\sum \frac{1}{N'_{\alpha\beta}} (x_\alpha^{(o)} - x_\beta^{(o)})^2 \tag{14}$$

and K_y and K_z have similar forms. If the rubber is isotropic on the average, there will be nothing to distinguish the three coordinates directions, and one will have $K_x = K_y = K_z = K/2$. We then write:

$$\mathfrak{C}(L_x, L_y, L_z) = K_1 \exp\{-\frac{K}{2}(L_x^2 + L_y^2 + L_z^2)\} \tag{15}$$

This equation, and more generally equation 11, states a very simple and interesting result: when an arbitrary network of Gaussian chains is subjected to uniform stretching in three coordinate directions, by corresponding displacement of its fixed points, the number of configurations possible for the system as a whole is a Gaussian function of its external dimensions. This result is not at all affected by the presence of loose ends or unattached material in the system, nor will these change K or the entropy forces exerted by the network.

Equations 4 and 15 yield the following expression for the entropy of a rectangular parallelepiped of rubber:

$$S = S_1(V,T) - \frac{kK}{2}(L_x^2 + L_y^2 + L_z^2) \tag{16}$$

where the constant $k \ln K_1$ has been absorbed into S_1.

Having arrived at expressions for U and S, we can derive the stress-strain relation for an ideal rubberlike material. We consider as before a rectangular parallelepiped of volume:

$$V = L_x L_y L_z \tag{17}$$

originally a unit cube, subject to total outward forces X, Y, and Z on the faces perpendicular to the three coordinate directions. The work done by the system when its dimensions undergo small changes is:

$$dW = -X\,dL_x - Y\,dL_y - Z\,dL_z \tag{18a}$$

the change in internal energy is:

$$dU = T\,dS + X\,dL_x + Y\,dL_y + Z\,dL_z \tag{18b}$$

and the change in the free energy (F = U - TS) is:

$$dF = -S\,dT + X\,dL_x + Y\,dL_y + Z\,dL_z \tag{18c}$$

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*These relations can be derived as consequences of the assumption that all forces are normal to the surfaces. In order to keep the argument here as simple as possible one may consider these equations as describing one possible type of surface constraint.

Thus:

$$X = \left(\frac{\partial F}{\partial L_x}\right)_{L_y, L_z, T} = \left(\frac{\partial U}{\partial L_x}\right)_{L_y, L_z, T} - T\left(\frac{\partial S}{\partial L_x}\right)_{L_y, L_z, T} \tag{19}$$

Similar equations hold for Y and Z. From equations 2 and 17 it follows that:

$$\left(\frac{\partial U}{\partial L_x}\right)_{L_y, L_z, T} = \left(\frac{\partial V}{\partial L_x}\right)_{L_y, L_z, T} \left(\frac{\partial U}{\partial V}\right)_T = L_y L_z \left(\frac{\partial U}{\partial V}\right)_T$$

Similarly:

$$\left(\frac{\partial S_1}{\partial L_x}\right)_{L_y, L_z, T} = L_y L_z \left(\frac{\partial S_1}{\partial V}\right)_T$$

By use of equation 16, equation 19 then becomes:

$$X = -\left\{-\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial S_1}{\partial V}\right)_T\right\} L_y L_z - kTKL_x \tag{20}$$

Now the quantity in brackets involves only terms which occur also in the internal energy and entropy of the liquidlike uncured material; it is in fact just the pressure in such a liquid:*

$$P = -\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial S_1}{\partial V}\right)_T \tag{21}$$

We then write:

$$X = -PL_yL_z + KkTL_x \tag{22a}$$

$$Y = -PL_zL_x + KkTL_y \tag{22b}$$

$$Z = -PL_xL_t + KkTL_x \tag{22c}$$

These equations express the forces exerted by the material, -X, -Y, -Z, as sums of two parts–the outward forces exerted by a hydrostatic pressure P acting on the respective face areas, and inward pulls (entropy forces exerted by the network) proportional to the extension of the material in the given direction.**

In the case of unilateral stretch in the z direction of material free from external pressure, one has $L_x = L_y$, X = Y = 0. Then, from equations 22a and 17, one has:

$$P = P_n = KkT/L_z \tag{23}$$

Thus, there is a hydrostatic pressure inside the material even when it is subject to no external pressure. This is due to the tendency of the network to take on configurations of higher entropy and smaller volume; it is an internal pressure arising from the tendency of the network to contract. Equation 22c, by use of equations 17 and 23, then becomes:

$$Z = KkT\left[L_z - \frac{V}{L_z^2}\right] \tag{24}$$

When an external pressure P_e is applied to the system, we may divide the force on the x-faces of the cuboid into two parts, one of hydrostatic origin, $-P_eL_y L_z$, and one of other origin, X':

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*The difference in sign in equations 19 and 21 is due to the fact that P gives a force tending to decrease V, whereas X is a force tending to increase L_x.

**The origin of these forces has been discussed from the point of view of kinetic theory in Reference 1.

$$X = X' - P_eL_yL_z$$

Equation 22a then becomes:

$$X' = -(P - P_e) L_yL_z + KkTL_x \qquad (22a')$$

Similar equations hold for Y' and Z'. If the material is subject to unilateral stretch under external pressure ($X' = Y' = 0$) one has as before:

$$P - P_e = P_n = KkT/L_z \qquad (23')$$

and:

$$Z' = KkT\,[L_z - V/L_z^2] \qquad (24')$$

Thus, equation 23 gives the internal pressure due to the network, and equation 24 gives the force required to bring the cuboid to length L_z, whether or not the material is subject to a hydrostatic pressure in addition. This result is valid whatever the change in volume of the material on stretching, or on change in temperature or hydrostatic pressure. As a first approximation one may write:

$$V = V_0\,[1 + \alpha\,(T - T_0) - \beta P]$$

or:

$$V = V_0\,[1 + \alpha\,(T - T_0) - \beta\,(P_e + P_n)] \qquad (25)$$

The compressibility of rubber is of the order of that of typical liquids, and the change of V with P_n during stretch is unimportant. On the other hand, the temperature dependence of the volume is of importance for the understanding of the thermoelastic properties of rubber.

Equation 24 gives a form of the stress-strain relation that is characteristic of molecular networks, so long as they can be treated as Gaussian. In particular, it is independent of the structure of the network. The magnitude of the forces, however, does depend on the structure of the network; it is changed, for instance, if the structure is modified by further cure of the material. To determine the constant K requires specification of the network structure, either in detail or in some statistical sense. The most realistic approach to the determination of the constant K or the rigidity of the material, as it depends on the factors which describe the state of cure of the material, seems to lie in a consideration of the process by which physically occurring networks are built up as cure proceeds. We have developed the theory of this process elsewhere (5), and have there discussed fully the relation of this treatment of the problem to that employed by other authors. Comments on this point will also be found in following sections.

II. MODIFICATION OF THEORY BY ASSUMPTION THAT NETWORK JUNCTIONS ARE FIXED IN SPACE

In the theoretical treatment of so complex a system as a piece of rubber it is always necessary to replace the physical system by a simplified model. In the preceding section we have discussed a model of rubber which is idealized in three principal ways: it is assumed (a) that the internal energy is independent of the form of the material, (b) that each segment of the network has a Gaussian configuration function, and (c) that the steric hindrances between the network segments change the entropy only by an additive constant (see Appendix A). On the other hand, full account is taken of the fact that the molecular segments are linked into a network, without its being necessary to assume that this network has any special form.

Other theories of rubber that employ definite models of the system have avoided consideration of the rubber network as a whole by introducing additional assumptions. The resulting simplifications of the model all depend on the more or less extensive use of the idea (explicit or implied) that the junctions of the network can be considered to occupy fixed positions in space–positions which change in some definite way as the material is deformed.

The idea that the network junctions occupy fixed positions in space has been most concretely expressed by Kuhn. His earlier papers (6) deal with a model of rubber which, in effect, consists of flexible molecular chains with fixed ends, mid-points, and quarter-points. In his more recent papers (7,8) he pictures bulk rubber as a network of molecular chains, but states (7) that the points at which the chains are linked together to form the network thereby "become fixed and are practically excluded from taking part in the Brownian motion... Only the chain elements lying between these knots can move freely to some extent." On this assumption, his earlier formalism is applicable to the new model without change, the fixed points of the molecular chains in his earlier theory being identified with the network junctions, or with other points where equivalent constraints are effective (7).

Flory and Rehner (9) have employed the same idea as a simplifying assumption, without insisting on its close correspondence to physical reality. They consider a portion of a network, or "cell," consisting of four molecular segments joined to each other at one end and with the other ends fixed at the four vertices of a regular tetrahedron. Thus, they consider a central junction that is not fixed in position, and four junctions that are fixed at the vertices of the tetrahedron. The idea of fixed network junctions is also implicit in the work of Treloar (10), who has modified Kuhn's formalism by treating only the end points of the chains as fixed.

In Section III we shall show that it is very far from true that the junctions are fixed in space; in fact, they have a Brownian motion that is almost as extensive as that of other elements of the network. On the other hand, we shall there give arguments which indicate that one can nevertheless compute the entropy correctly on the basis of this assumption. In the present section we shall therefore carry through such a derivation, one which is simpler than those usually given, and which seems to us to make clearer the essential ideas of the calculation.

If the junctions of the network are essentially fixed, each segment of the network will have a fixed extension determined by the external form of the material alone. If, as in Section I, we consider a unit cube of rubber stretched into a cuboid with edges L_x,L_y, and L_z, then the extensions of the $\tau\nu$ segment will be:

$$r_{\tau\nu}(L_X, L_y, L_Z) = \{(x_\tau - x_\nu)^2 + (y_\tau - y_\nu)^2 + (z_\tau - z_\nu)^2\}^{1/2} \tag{26}$$

If steric hindrances between the segment are neglected, these segments become effectively independent systems: the number of configurations possible for the whole network can be computed simply as the product of the numbers of configurations which can be assumed by the component segments:

$$\mathfrak{C}(L_x,L_y,L_z) = C_0 \prod_{\tau>\nu}\prod \exp\left\{-\frac{3}{2l^2 N_{\tau\nu}}\, r_{\tau\nu}^2\right\} \tag{27}$$

The entropy of the system is then:

$$\begin{aligned} S(L_x,L_y,L_z) &= S_1(V,T) + k \ln \mathfrak{C}(L_x,L_y,L_z) \\ &= S_1(V,T) + k \ln C_0 - \frac{3k}{2l^2} \sum_{\tau>\nu}\sum \frac{1}{N_{\tau\nu}}\, r_{\tau\nu}^2(L_x,L_y,L_z) \end{aligned} \tag{28}$$

where the last and most important term is the sum of contributions from the individual segments, as though they were independent. The next essential assumption in the calculation, common to all theories in which the junctions are treated as fixed in space, is that the coordinates of all junctions change according to the law:

$$x_\tau = x_\tau^{(o)} L_x \qquad y_\tau = y_\tau^{(o)} L_y \qquad z_\tau = z_\tau^{(o)} L_z \tag{29}$$

when the material is deformed. In Section I, similar equations described the motion of the points of the network that were subject to external constraint; here, the assumption applies to all junctions, however remote from external constraints. By equations 26 and 29, equation 28 becomes:

$$S(L_x,L_y,L_z) = S_1(V,T) - k\{K_x L_x^2 + K_y L_y^2 + K_z L_z^2\} \tag{30}$$

where:

$$K_x = \frac{3}{2l^2} \sum_{\tau>\nu}\sum \frac{1}{N_{\tau\nu}} (x_\tau^{(o)} - x_\nu^{(o)})^2 \tag{31}$$

K_y and K_z have similar forms. The constant $k \ln C_0$ has been absorbed into S_1. If the undeformed material is isotropic on the average, then $K_x = K_y = K_z = K/2$, and one has again equation 16.

$$S(L_x,L_y,L_z) = S_1(V,T) - \frac{kK}{2}(L_x^2 + L_y^2 + L_z^2) \tag{16}$$

To establish a definite value of K it is necessary to introduce further assumptions into the theory. It follows from equation 31 and the assumption of isotropy that:

$$\begin{aligned} K &= \frac{2}{3}(K_x + K_y + K_z) \\ &= \frac{1}{l^2} \sum_{\tau>\nu}\sum \frac{1}{N_{\tau\nu}} \{(x_\tau^{(o)} - x_\nu^{(o)})^2 + (y_\tau^{(o)} - y_\nu^{(o)})^2 + (z_\tau^{(o)} - z_\nu^{(o)})^2\} \\ &= \frac{1}{l^2} \sum_{\tau>\nu}\sum [r_{\tau\nu}^{(o)}]^2 / N_{\tau\nu} \end{aligned} \tag{32}$$

where $r_{\tau\nu}^{(o)}$ is the extension of the $\tau\nu$ segment when the material is unstretched. Here K appears as a sum of contributions from the component segments of the network. If we define:

$$\lambda_{\tau\nu}^{(o)} = r_{\tau\nu}^{(o)} / l N_{\tau\nu} \tag{33}$$

the fractional extension of the $\tau\nu$ segment in the unstretched material, we can also write:

$$K = \sum_{\tau>\nu}\sum N_{\tau\nu} [\lambda_{\tau\nu}^{(o)}]^2 \tag{34}$$

It is thus evident that K does not depend on the detailed structure of the network, but only on the number of segments with a given number of links, and on their fractional extensions when the material is unstretched. If $F(N)dN$ is the number of segments per unit volume for which the number of links lies between N and N + dN, and $G(N,\lambda)\,d\lambda$ is the fraction of these segments which have fractional extensions between λ and $\lambda + d\lambda$, then:

$$K = \int_0^\infty dN \int_0^1 d\lambda \quad F(N)\, G(N,\lambda)\ N\lambda^2 \tag{35}$$

Theories which assume fixed network junctions usually include some additional hypotheses which serve to fix the distribution functions F(N) and $G(N,\lambda)$. The most common assumption, originally due to Wall (2), is that the extensions of the molecules have the same distribution as would be found in a system of unconstrained molecules subject to thermal agitation. From this assumption it follows that:

$$G(N,\lambda) = \frac{4}{\pi^{1/2}}\left(\frac{3N}{2}\right)^{3/2} \lambda^2 \exp\{-\frac{3}{2}N\lambda^2\} \tag{36}$$

On carrying out the integration in equation 35 one finds K = G, the total number of segments per unit volume in the network, whatever the form of F(N). Other assumptions lead to different forms of $G(N,\lambda)$, and to other values of K. The significance of this approach to the determination of K, and of the rigidity of a material, is discussed at length in Section II of Reference 5.

III. ARE NETWORK JUNCTIONS REALLY FIXED IN SPACE?

It now becomes necessary to examine the justification of Kuhn's assumption that the network junctions occupy effectively fixed positions in space. Kuhn gives no detailed argument in support of this idea; his acceptance of it seems to be based on a qualitative picture of the situation. We shall now show that this assumption is very unrealistic—that the junctions, in fact, have a Brownian motion comparable to that of other elements of the network.

The coupling together of two elements of a network to form a new junction of the network does decrease the extent of the Brownian motion of these elements. This can be discussed quantitatively as follows.

It has been shown by James (4) that the number of configurations of an arbitrary Gaussian network consistent with element i having coordinates x_i, y_i, and z_i is:

$$\mathfrak{C}_i(x_i,y_i,z_i) = c_i \exp\{-\frac{3}{2l^2\mathfrak{J}_i}[(x_i-x_{oi})^2 + (y_i-y_{oi})^2 + (z_i-z_{oi})^2]\} \tag{37}$$

where x_{oi}, y_{oi}, z_{oi}, and $\mathfrak{J}_i$ are constants. The probability that the Brownian motion of the network will bring element i to the point (x_i,y_i,z_i) is proportional to $\mathfrak{C}_i$; if we write:

$$P_i(x_i,y_i,z_i) = \{3/2\pi l^2\mathfrak{J}_i\}^{3/2} \exp\{-(3/2l^2\mathfrak{J}_i)[(x_i-x_{oi})^2 + (y_i-y_{oi})^2 + (z_i-z_{oi})^2]\} \tag{38}$$

then the probability that element i will lie in a volume dV about the point x_i,y_i,z_i is:

$$dP = P_i\ (x_i,y_i,z_i)\ dV \tag{39}$$

Obviously, then, x_{0i}, y_{0i}, z_{0i} are the most probable values of these coordinates. The rms distance of the element from its most probable position is $\mathfrak{J}_i^{1/2} l$; thus $\mathfrak{J}_i^{1/2}$ will serve as a measure of the extent of the Brownian motion of the element.

Let j be a second element of the network, with a mean deviation $\mathfrak{J}_j^{1/2} l$ from a most probable position (x_{0j}, y_{0j}, z_{0j}); its probability distribution will have the form of equation 38, except for a change in subscripts. Now let elements i and j be linked together permanently by a bond formed when they happen to lie near each other. Together, these elements will then constitute a junction in a modified network, with a probability distribution function:

$$P(x,y,z) = \{3/2\pi l^2 \mathfrak{J}_{i+j}\}^{3/2} \exp\{-(3/2l^2 \mathfrak{J}_{i+j})[(x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2]\} \qquad (40)$$

The most probable position of the new junction, (x_0, y_0, z_0), can be shown to lie on the line between the former most probable positions of the separate elements; the fluctuations in position of the junction are proportional to $\mathfrak{J}_{i+j}^{1/2}$.

It is easy to show that, if the elements i and j had independent Brownian motion before they were bonded together, then:

$$\frac{1}{\mathfrak{J}_{i+j}} = \frac{1}{\mathfrak{J}_i} + \frac{1}{\mathfrak{J}_j} \qquad (41)$$

In general, however, these two elements will have been more or less closely coupled together in the network structure, and equation 41 will not apply. In such cases the value of $\mathfrak{J}_{i+j}$ depends on $\mathfrak{J}_i$ and $\mathfrak{J}_j$, but also on the fluctuation in the relative coordinates of elements i and j in the original network. It is shown in reference (4) that this fluctuation is described by a Gaussian distribution function:

$$R_{ij}(\xi,\eta,\zeta) = \left\{\frac{3}{2\pi l^2 \mathfrak{J}_{ij}}\right\}^{3/2} \exp\{-(3/2l^2 \mathfrak{J}_{ij})[(\xi-\xi_0)^2 + (\eta-\eta_0)^2 + (\zeta-\zeta_0)^2]\} \qquad (42)$$

where ξ, η, and ζ are the relative coordinates of the elements and ξ_0, η_0, and ζ_0, are the most probable values of these relative coordinates [$\xi_0 = x_{0i} - x_{0j}$, etc.] The fluctuations in the relative positions of the elements are thus proportional to $\mathfrak{J}_{ij}^{1/2}$. It can be shown that:

$$\mathfrak{J}_i + \mathfrak{J}_j \geq \mathfrak{J}_{ij} \geq |\mathfrak{J}_i - \mathfrak{J}_j| \qquad (43)$$

When the elements are independent,

$$\mathfrak{J}_{ij} = \mathfrak{J}_i + \mathfrak{J}_j \qquad (44)$$

The calculation of $\mathfrak{J}_{i+j}$ in the general case can be made as follows. Before the bond is formed between elements i and j, the number of configurations of the network for which x_i and x_j have specified values in proportional to:

$$\exp\left\{-\frac{6}{l^2}\,\frac{\mathfrak{J}_j(x_i-x_{0i})^2 + [\mathfrak{J}_{ij}-\mathfrak{J}_i-\mathfrak{J}_j](x_i-x_{0i})(x_j-x_{0j}) + \mathfrak{J}_i(x_j-x_{0j})^2}{2\mathfrak{J}_i\mathfrak{J}_j + 2\mathfrak{J}_i\mathfrak{J}_{ij} + 2\mathfrak{J}_j\mathfrak{J}_{ij} - \mathfrak{J}_i^2 - \mathfrak{J}_j^2 - \mathfrak{J}_{ij}^2}\right\} \qquad (45)$$

This follows easily from equation 6.2 of reference 4, by use of equations 5.4, 6.6, and 7.6. After the bond is formed, only those configurations are possible for which $x_i = x_j = x$. On making this substitution into equation 45 and rearranging terms, one finds that their number is proportional to:

$$\exp\left\{-\frac{6}{l^2}\,\frac{\eta_{ij}\left\langle x-(1/2\eta_{ij})([\eta_{ij}+\eta_j-\eta_i]x_{0i}+[\eta_{ij}+\eta_i-\eta_j]x_{0j})\right\rangle^2}{2\eta_i\eta_j+2\eta_i\eta_{ij}+2\eta_j\eta_{ij}-\eta_i^2-\eta_j^2-\eta_{ij}^2}\right. \tag{46}$$

The probability of finding the new junction with coordinates x is proportional to this number; the probability of finding it with coordinates x,y, z is the product of three such factors, differing only in the substitution of y or z for x. Thus, the normalized probability distribution can be written as in equation 40, with:

$$x_0 = ([\eta_{ij}+\eta_j-\eta_i]x_{0i}+[\eta_{ij}+\eta_i-\eta_j]x_{0j})/2\eta_{ij} \tag{47}$$

and:

$$\begin{aligned}\eta_{i+j} &= (2\eta_i\eta_j+2\eta_i\eta_{ij}+2\eta_j\eta_{ij}-\eta_i^2-\eta_j^2-\eta_{ij}^2)/4\eta_{ij}\\ &= \eta_i-(\eta_{ij}+\eta_i-\eta_j)^2/4\eta_{ij}\\ &= \eta_j-(\eta_{ij}+\eta_j-\eta_i)^2/4\eta_{ij}\end{aligned} \tag{48}$$

It is thus proved that η_{ij} is always less than η_i or η_j and that the Brownian motion of the new junction is less than that of the unbonded elements.

Formation of a bond between two elements of a network will not merely reduce the Brownian motion of the bonded elements: it will also reduce the Brownian motion of all nearby elements of the network. Kuhn assumes that the Brownian motion of the junctions of the network will become very much less than that of elements of the intervening chain segments, but this does not follow from the foregoing proof. This point also is susceptible to a general quantitative discussion. Let points i and j be junctions of the network connected by a segment with M links, and let k be an element of this intervening segment, distant from junction i by N_i links and from junction j by $N_j = M - N_i$ links. The distribution function for this intermediate element is of the form of equation 38, with the subscript k replacing the subscript i. The intermediate element will thus have a Brownian motion proportional to $\eta_k^{1/2}$ about a most probable position, which is easily seen by the methods in Section VIII of reference 4 to be given by:

$$x_{0k} = (N_j\, x_{0i} + N_i\, x_{0j})\ /\ (N_i + N_j),\ \text{etc.} \tag{49}$$

It is shown in Appendix B of the present paper that:

$$\eta_k = \frac{N_iN_j}{N_i+N_j}\left\{1+\frac{\eta_i}{N_i}+\frac{\eta_j}{N_j}-\frac{\eta_{ij}}{N_i+N_j}\right\} \tag{50}$$

η_k approaches η_i as $N_i \rightarrow 0$, and approaches η_j as $N_j \rightarrow 0$; between these limits it passes through a maximum.

A convenient illustration of the relative magnitudes of these quantities is provided by the regular cubic network discussed in Section IX of reference 4. This consists of segments, each containing M links, joined together with the connectivity of a cubic lattice; each junction, then, is the point of union of six segments. It is shown in Reference 4 that for junctions of this network not too near the fixed points one has:

$$\eta_i \cong \eta_j \cong M/4 \tag{51}$$

If i and j are adjacent junctions:

$$\mathfrak{h}_{ij} \cong (M/2)(1-\pi^{-1}) \tag{52}$$

Since $\mathfrak{h}_i = \mathfrak{h}_j$ for this network, $\mathfrak{h}_k$ takes on its maximum value for the element midway between the junctions: $N_i = N_j = M/2$. For this element one has, by equation 50:

$$\mathfrak{h}_k \cong \frac{3 + 1/\pi}{8} M = 1.66\mathfrak{h}_i \tag{53}$$

It follows easily that in this network the mean fluctuation of the junction coordinates is only 23% less than that of the midpoints of the segments. In addition, it should be emphasized that the difference would be expected to be greater in this model, where each junction is under constraint by six segments, than in a network in which only three or four segments end at each junction. In general, then, one cannot expect that the junctions of molecular networks will have a Brownian motion which is very much less than that of other elements of the network.

It is, nevertheless, a striking fact that one obtains the same stress-strain relation whether or not one assumes that the junctions are essentially fixed in space. The form of the relation is always the same; the identity of the results extends even to the magnitude of the stress if the assumed fixed positions of the junctions are identical with their actual most probable positions.*

The identity of these results was first indicated by us, in the Appendix of an earlier paper (1). It was there shown that the junctions of an arbitrary Gaussian network have most probable positions which vary according to equation 29, when the fixed points of the network are subjected to displacements of the same homogeneous type. It was also shown that the forces exerted by the network will be unchanged if any movable junction (or other point) of the network is fixed at what would otherwise be only its most probable position. It follows that the computed stress will be unchanged if one treats any or all of the actually movable junctions as fixed at its most probable position. This detailed analysis of the system is useful for many purposes, but it makes the identity of the results of the two types of calculation appear as a consequence of special properties of the Gaussian function.

An understanding of the identity of these results can be based on more general grounds by making use of the idea of distributions of configurations (11). One can divide all space into domains, not too many in number, such that there will be an equal probability that junction i will lie in each of these domains; we may denote these domains by $V_{i\tau}$, $\tau = 1,2,3...$ A different division of space into domains $V_{j\tau}$ appropriate to junction j can be made. A "distribution of configurations" of the network will include all configurations in which junction i lies in a specified domain $V_{i\tau}$, junction j in a specified domain $V_{j\nu}$, and

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*For instance, equation 17 of reference 5, derived on the basis of the general network theory, is identical in form with equation 34 of this paper, derived on the assumption that the junctions are fixed; in the first equation $\lambda^{(0)}_{\tau\nu}$ is defined in terms of the most probable positions of movable junctions τ and ν, whereas in the second it is correspondingly defined in terms of the positions of fixed junctions.

so on. If the number of configurations possible for the network segments is sufficiently large compared with the number of junctions in the network, the total number of distributions will be small compared to the number of possible configurations of the network. Now the most probable configuration of the junctions is that in which each junction lies at its most probable position (4). The most probable distribution will, correspondingly, be that in which each junction lies in the domain which includes its most probable position. The number of configurations in this distribution will differ from the total number of configurations by a factor which is very small as compared with that total number. In computing the entropy, proportional to the logarithm of the number of configurations, one will then make only a small error if one counts only the configurations in the most probable distribution-configurations in which each junction lies near its most probable position. In the derivation of results that are valid for networks with small numbers of junctions (such as those with which we are here concerned) it is possible to carry this process to the limit of treating each junction as fixed at its most probable position: with such networks one can reasonably define distributions in which the position of each junction is very accurately specified. In other words, it is possible to treat the junctions as fixed in deriving results that depend on the statistical behavior of the links as components of the segments, but not on the statistical behavior of segments as components of the network. One may compare such a treatment to a calculation of the pressure of a gas based on the idea that one will find exactly half of the molecules in a given half of the volume at any given time. The result of the calculation will be correct, though the assumed restriction has no analog in nature, and one is in fact considering only a small fraction of the configurations which the system can assume.

The possibility of treating the network junctions as fixed in calculations of this type does not imply that a similar procedure will be possible when other properties of the system are to be discussed. This assumption should be avoided–as indeed it can be without much trouble–in discussing details in the behavior of the network. It would, for instance, be quite out of place in a discussion of the change of network structure during cure.

IV. WALL'S THEORY OF RUBBER

Wall (12-14) has derived a stress-strain relation for rubber:

$$Z = GkT\,[L_z - 1/L_z^2] \tag{54}$$

without making use of any definite model of the system. His theory is often referred to as a network theory of rubber, and Wall himself (13,14) indicates that his calculations apply to rubber considered as a molecular network.

Wall's theory is not a typical application of statistical mechanics. In a statistical theory one usually starts from a definite model of the physical system, with specified statistical weights, constraints, potential fields, and so on. On this basis one then derives distribution functions which describe the system statistically; from these one can finally compute average or observable properties of the system. Wall, on the other hand, does not describe his model, and postulates rather than describes his distribution functions. His postulates do not have a general validity which would bestow a like general validity on his results; instead, they correspond to a special model of unspecified type, the nature of which one can only infer from the character of the postulates. We shall now show that Wall's mathematical postulates are inconsistent with the network structure of rubber, and that his theory can lead to results different from those given by the network theory.

Wall's procedure is indicated in most detail in the one-dimensional treatment of his first paper, but even there it is not completely explicit. In essence it involves the following steps. The notation is that of Wall's paper (12).

(1) It is assumed that the molecules are of uniform length, with Gaussian configuration functions.

(2) It is assumed that when the bulk material is unstretched the distribution function for extensions of the chains (displacements between the end points) is of the same form as the configuration function, but normalized to 1. In the one-dimensional case the distribution of extensions x is given by:

$$p(x) = \frac{\beta}{\pi^{1/2}} \exp\{-\beta^2 x^2\} \tag{55}$$

(3) It is postulated that when the material is stretched the distribution function is modified in a particular way (13): "The components of the lengths of the individual molecules will change in the same ratio as does the corresponding dimension of the piece of rubber." In the one dimensional case the distribution function becomes:

$$p'(x) = \frac{\beta}{\alpha\pi^{1/2}} \exp\{-\beta^2 x^2/\alpha^2\} \tag{56}$$

α being the ratio of the extended length to the unstretched length of the material.

(4) The relative probability of the states described by these distribution functions (i.e., the relative number of configurations of the system consistent with the specified distributions of chain extension) is then computed as follows: The range of values of the extensions is divided into small regions, the ith of which, about $x = x_i$, is of length Δx_i. Then:

$$p_i = p(x_i)\Delta x_i \tag{57}$$

is the relative number of configurations for a chain of extension x_i to within Δx_i. When the material is unstretched, the average number of chains out of a total number N, which have extensions in the range Δx_i, is:

$$n_i = Np_i = Np(x_i)\Delta x_i \tag{58}$$

When the material is stretched, the average number of chains with extensions in the range Δx_i is:

$$s_i = N\, p'(x_i)\Delta x_i \tag{59}$$

The relative probability of the distribution (equation 56) for the stretched material is then computed as:

$$P = N! \prod_i \frac{p_i^{s_i}}{s_i!} \tag{60}$$

which reduces, as stretch of the material is reduced to zero, to:

$$P_0 = N! \prod_i \frac{p_i^{n_i}}{n_i!} \tag{61}$$

(5) The change of entropy of the material on stretching is then taken to be:

$$S - S_0 = k \ln (P/P_0) \tag{62}$$

We have now to examine some of the implications of this formalism.

The distribution functions of Wall's theory imply that there exist certain unspecified constraints on the extension of the molecules. Since p(x) is of the same form as the configuration function, it would describe the distribution of extensions for a system of independent, unconstrained molecules; this is not, however, a possible model for the system, for in the absence of constraints on or between the molecules the distribution function would be independent of the form of the material, and the theory would predict no restoring forces. The function p(x) will also describe a model formed by freezing the ends of the molecules into fixed positions, either simultaneously or at random times. This same model will also yield Wall's postulated distribution functions for the stretched material (p′(x) in the one-dimensional case) if the fixed positions of the ends of the chains are supposed to change according to equation 29. Indeed, the quotation from Wall's second paper (13), as given under (3) above, seems to indicate that he had such a model in mind.

Wall's distribution functions would also describe a network with fixed junctions formed by the union of his "molecules" at their ends–a model in which each "molecule" becomes a segment of the network. Wall's postulates do not apply to a general model of this type, for they establish also the distribution of the fixed fractional extensions of the segments, which, in the three-dimensional case, is essentially that of equation 36. They thus serve to determine the value of the factor K in the stress–strain relation, as discussed in Section II.

The further development of Wall's calculation is, however, inconsistent with any of the models mentioned above. If each molecule has a definite extension, changing in a definite way when the material is stretched, the relative number of configurations accessible to the system is (cf. eq. 27):

$$P = \prod_i p_i^{s_i} \tag{63}$$

In equation 60 there appears an additional factor $(N!/\prod s_i!)$. This is the number of different ways in which the specified set of chain extensions can be assigned to the molecules, provided that each molecule can take on any extension independently of the extensions of the other molecules. The presence of this factor is inconsistent with the assumption of fixed extensions for the segments. It is also inconsistent with the assumption that the molecules are joined together to form a network, for their connection into a network would establish certain relations between the segment extensions.

In his third paper (14) Wall has attempted to show that the distributions of equations 55 and 56 apply to a system of molecules linked to form a network with movable junctions. However, his discussion and conclusions appear to be incorrect. The distribution function for the components ξ, η, and ζ of the extension of any segment of any Gaussian network is of the form of equation 42. It is a Gaussian distribution about mean values ξ_0, η_0, and ζ_0 of the components; these mean values change as the network is stretched, but the breadth of the distribution, determined by $\mathfrak{J}_{ij}$, does not. Wall's distribution is of a quite different character, being a Gaussian distribution about fixed mean values (0 for each component), which changes in breadth when the material is stretched.

The argument in Wall's third paper (14) will be indicated briefly. Wall restricts his consideration to the simplest possible network, a one-dimensional chain of N molecules with identical Gaussian configuration functions, like that of equation 55. The distribution function for molecular extensions describes the most probable distribution of molecular extensions consistent with the fixed total extension of the chain, which will here be called L. The relative number of molecular configurations consistent with the assignment of N_0 molecules to the range Δx_0 of extensions, N_i molecules to the range Δx_i etc., is:

$$W = \frac{N!}{N_0!\ N_1!\ N_2!\ldots}\ p_0^{N_0}\ p_1^{N_1} p_2^{N_2}\ldots \tag{64}$$

To determine the distribution function $N_i(x_i)$ one has to choose the N_i so as to maximize this expression, subject to two conditions of constraint: the total number of molecules is N, and the total extension of the chain is L. In symbols,

$$N = \sum_i N_i \tag{65}$$

and:

$$L = \sum_i N_i x_i \tag{66}$$

Solution of this problem leads to the correct distribution function:

$$p'(x) = \frac{\beta}{\pi^{1/2}} \exp\left\{- \beta^2 (x - L/N)^2\right\} \tag{67}$$

Instead, Wall replaces equation 66, obviously required by his statement of the problem, by a different condition of constraint:

$$L^2 = C \sum_i N_i x_i^2 \tag{68}$$

and finds the erroneous distribution function:

$$p'(x) = \left(\frac{CN}{2\pi L^2}\right)^{1/2} \exp\left(- \frac{CN}{2L^2} x^2\right) \tag{69}$$

which has a quite different character. Wall arrives at equation 68 in the following way. In a preliminary discussion of the chain of molecules he concludes that:

$$\left\langle x_i^2 \right\rangle_{av} = L^2/N \tag{70}$$

where $\langle x_i^2 \rangle_{av}$ is the mean square extension of any molecule in the chain. This he rewrites, with the addition of an arbitrary constant factor C, to obtain equation 69. However, in deriving equation 70, he neglects terms which are individually small (of the order of L^2/N^2) but so numerous that in the aggregate they far outweigh the terms which he retains. An exact discussion of the problem yields:

$$\langle x_i^2 \rangle_{av} = \frac{L^2}{N^2} + \frac{1}{2\beta^2} \tag{71}$$

which differs from equation 70 by a large and variable factor. It will be noted that equations 68 and 70 imply that when the chain of molecules has total extension zero every molecule in the chain must have total extension zero—an obviously false result. Correspondingly, the distribution function of equation 69 gives for every molecule $\langle x_i \rangle_{av} = 0$, whereas the correct value must be L/N; this value is of course given by equation 67.

The additional factor in equation 60, as compared to equation 63, leads to the presence in Wall's theory of a term in the entropy which has no analog in the theory of a Gaussian network. In the one-dimensional case the network theory, with Wall's distribution functions for a system of G molecules, gives:

$$S - S_0 = -\frac{G}{2}\alpha^2 \tag{72}$$

whereas Wall's computation yields:

$$S - S_0 = G \ln \alpha - \frac{G}{2}\alpha^2 \tag{73}$$

Correspondingly, the one-dimensional network theory leads to the stress-strain relation:

$$Z = GkT\alpha \tag{74}$$

but Wall's computation yields:

$$Z = GkT(\alpha - \frac{1}{\alpha}) \tag{75}$$

Wall's theory thus leads to a non-zero length for the system under zero external force. On the other hand, the network theory gives zero length for zero external force; with a one-dimensional network, as with a single Gaussian chain, it requires a non-zero average force to keep the ends of the system at a fixed finite separation, however small.* Neither one-dimensional model is suitable for discussion of the characteristics of the real three-dimensional networks; when the theory is extended to three dimensions it is the network model that corresponds more closely to reality.

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*Thus, when equation 63 is used, $\alpha = 1$ does not represent the case of zero external force. Some confusion has arisen in this connection. Because a molecule under zero external force has non-zero mean square extension, it has been assumed that a calculation of the stress-strain relation must yield a non-zero "natural length" for the molecule under zero external force. Whether or not this is the case will depend on how terms are defined. If the stress-strain relation is defined in terms of the rms extension of a system under constant external force one will find a non-zero "length" for zero force. If, however, one defines the stress-strain relation in forms of the average force required to maintain a constant extension, then the force to zero only as the length goes to zero. It is the latter point of view that is implicit in the calculation of the entropy as a function of the fixed extension of the molecular chain, and the derivation of the force Z from this entropy

In three dimensions, Wall's method of calculation would again yield, in general, an additional term in the entropy:

$$\Delta S = G \ln (\alpha_x \alpha_y \alpha_z) \tag{76}$$

where α_x, α_y, α_z are the relative extensions in the x,y,z directions, respectively. This term does not appear in Wall's second paper, being suppressed by his immediate assumption that the material is incompressible: $\alpha_x \alpha_y \alpha_z = 1$. Thus, Wall's treatment yields the same result as the network theory in this special ease. The difference between the theories would become evident if compressibility were taken into account, and would be particularly important in a discussion of the swelling of rubber.

It is clear that Wall's formalism cannot be interpreted in terms of any system consisting of flexible molecular chains alone. We have not been able to devise any model to which it can properly be applied. We believe, therefore, that Wall's method of calculation, and particularly the use of equations 60 and 61, should be avoided as lacking physical significance.

This criticism applies also to the work of Kuhn and Kuhn (8), who have pictured rubber as a system of molecular segments with movable ends, and have calculated its entropy by a method similar to that of Wall. They divide the entropy into two parts, one associated with the orientation of the segments, the other with their extensions, and calculate these quantities as though each segment could take on any given orientation and extension with the same probability as any other segment. It should hardly need further emphasis that this is not the case if the segments are connected into a network. The calculation of Kuhn and Kuhn, like that of Wall, yields the same result as the network theory for the special case of a distortion at constant volume.

We have elsewhere (5) discussed our objections to Wall's assumed distribution functions (such as that of equation 56) as descriptions of the mean fractional extensions of segments in physically occurring networks.

APPENDIX A

Justification of Neglect of Steric Hindrances

In using a Gaussian network as a model for the actual molecular network of rubber, one is not neglecting steric hindrances entirely. The fixed points of the model, representing the points of the real network to which external forces are applied, have been constrained to lie on the external surfaces of the material—in positions which are in fact largely determined by the volume-filling property of the molecules through the form of U(V,T). When computing the entropy of the system by enumerating configurations of the network, one is consequently limited to the counting of network configurations which extend through a volume in space determined by the steric hindrances. Hence one does not consider, in a way which would make senseless the outcome of the calculation, the very numerous configurations of very small volume which might be assumed by an idealized network without volume-filling properties and without fixed points. In other words, calculation with this model includes enumeration of only those configurations with the correct average density of chain elements in space.

The steric hindrances of real molecular chains do not merely exclude configurations of the system in which the average density is abnormal; they prevent also the realization of all configurations of the system in which any two portions of molecular chain occupy the same volume in space. In our treatment of the idealized network the details of the configurations are not specified completely enough to permit exclusion of these configurations, which are consequently included in the counting. We have now to indicate the consequences of thus taking into account the volume-filling properties of the molecules on the average, but not in detail.

For this discussion we distinguish between transient and permanent constraints. By a "transient constraint" we mean one that does not permanently exclude any configuration of the system that would otherwise be possible, nor give to it a weight different from that of any other possible configuration with the same energy. Typical of transient constraints are those imposed upon a flexible molecular chain immersed in an (idealized) liquid of foreign, or even similar, molecules. The molecules of this liquid subject the given molecule to constraints which vary from instant to instant, excluding by their volume-filling properties now this configuration of the molecule, now that; nevertheless, in the course of a sufficiently long period, they would permit this given molecule to take on all the configurations which it could assume in their absence, and with the same relative probability. A "permanent constraint," on the other hand, is one which permanently changes the relative probability of occurrence of certain configurations or makes them impossible of realization. Union of molecules into a coherent network, or the establishment of fixed points of a molecular network, are examples of permanent constraints.

A single flexible molecular chain with ends fixed at separation L exerts against these constraints an average force Z given by the familiar equation:

$$Z = -kT \frac{d}{dL} \ln c(L)$$

where c(L) is the number of configurations consistent with the given L — or, more generally, the sum of the statistical weights of the possible configurations. The fixing of L is of course a permanent constraint on the chain. If other constraints are present they will modify c(L) by excluding some configurations from consideration, or changing their statistical weights. If these constraints have an effect which varies in time, c(L), like Z, is to be taken as an average value over a long period.

An important special class of constraints has the property of changing c(L) by a constant factor, as by excluding from consideration a constant fraction of the configurations that would otherwise be possible, or by changing their statistical weights by a constant factor; such constraints leave $\langle Z\rangle_{av}$ completely unchanged. Transient constraints, as defined above, are of this type. Thus, Z will be the same for a chain whether it is in thermal equilibrium with a tenuous gas, or with a surrounding liquid, so long as the period of averaging the force is sufficiently long for the constraints imposed by the liquid to have a transient character. The result is the same when one averages, not over a considerable time, but over a large number of similar chains and a correspondingly shorter time—as one actually does in observing bulk rubber.

In a liquid of rubber molecules the volume-filling property of the molecules causes them to exert constraints on each other, but only transient ones. This situation is largely unaltered when the material is vulcanized. To the extent to which each chain moves as in a fluid composed of the other chains, our treatment is complete: equation 7 continues to give the relative number of configurations of each segment as a function of the separation of its ends, and the computation proceeds as before. To this approximation the volume-filling property of the chains reduces the number of configurations of the network by a factor which is independent of the form of the material; it modifies only the value of the constant K_1 in equation 15, and not the forces exerted by the system.

A more detailed, and in some respects more satisfying, analysis of the effects of volume-filling can be carried out by the methods of the Appendix in a previous paper (1), which fixes attention on the forces acting within the network, as well as on those exerted by the network against external constraints. It is there shown that:

(a) The mean position of each junction of a Gaussian network is the position at which it would be subject to zero average force (due to the chains which enter it) if it were fixed there, and

(b) The average force which the network exerts on any fixed point can be computed as the sum of the average forces exerted on it by all the segments which enter it, when all junctions of the network are treated as fixed at their most probable positions.

To the approximation in which any segment is subject only to transient constraints by the liquidlike mass of other segments in which it is embedded, the average force exerted by that segment is unchanged by the presence of the other segments. If this assumption is extended to all segments, it follows from (a) that the mean positions of the network junctions are unchanged by these transient constraints, and then from (b) that the average force on each fixed point of the network—and hence the net force which we have computed in section I—is unchanged.

However, not all the constraints arising from steric hindrances are of transient character. For instance, when two molecules are linked at a junction there will arise steric hindrances of the permanent type; the effect of these will be, essentially, to reduce the flexibility of the molecular segments in the immediate neighborhood of the junction. So long as one restricts attention to lightly vulcanized materials, in which only a relatively small portion of the total chain length is near to any junction, one is justified in neglecting this type of steric hindrance. On the other hand, it will become an extremely important factor in the behavior of highly vulcanized hard rubbers.

A more interesting type of steric hindrance comes into play when the network is formed as illustrated in Figure 2. Sketches (a) and (b) illustrate possible structures in which chains of the same length connect similar junctions in essentially different ways. In our discussion such different structures have received identical treatment, even though, considered in detail, the configurations possible for one structure are impossible for the other. The effect of neglecting such steric hindrances will vary markedly with the structure of the network and its condition of stretch. If the segments are long as compared with the distances between their ends, as illustrated in Figure 2(c), the constraints exerted by one segment on the other will be almost completely of the transient type, causing but little change in the forces exerted by the network. This is the situation typical of lightly vulcanized materials at small extensions. If one segment is tightly drawn over the other, as in Figure 2(d), the effect of the entanglement will be almost the same as if the molecules were bonded together in the region of their crossing. Such a condition is very unlikely to occur in an unstretched material. The relation of the molecules is one of very low probability, one unlikely to occur in the material undergoing vulcanization and correspondingly unlikely to be built into the network as it is formed. On the other hand, a situation of type (c) can be converted into one of type (d) if the material is highly extended. Our neglect of these steric hindrances can thus be justified for lightly vulcanized materials not too highly extended; at high extensions these steric hindrances may contribute markedly to the rigidity of the material. This is, however, a range in which the configuration functions of the segments can no longer be treated as Gaussian, and the theory outlined in this paper cannot be expected to apply.

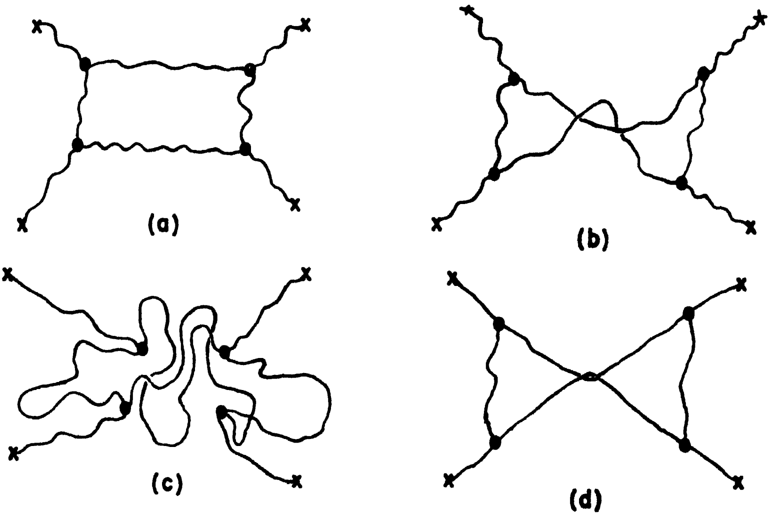

Fig. 2. Diagram illustrating action of steric hindrances. In (b),(c),(d), the lower chain is to be understood as passing around the upper one. Fixed points (×); junctions (●).

APPENDIX B

Brownian Motion of Intermediate Points of a Chain

The Brownian motion of the intermediate points of a chain segment can be related to the Brownian motion of its ends by an analysis of the sort employed earlier (4), and in section III of this paper. A more compact proof will be given here. The notation is that of a previous paper (4).

We consider a segment with $N_i + N_j$ links. Let the terminal elements i and j of the segment be assigned the highest number, n - 1 and n, in the numbering of the junctions of the network. Without loss of generality it can be assumed that the segment with which we are concerned is the only one which passes from i to j without passing through some other junction; if any other connections between i and j exist, one can pick some element of each segment for treatment as a junction, as is explained elsewhere (4). The lower right corner of the Γ determinant then has the following appearance:

$$\Gamma = \begin{vmatrix} \cdot & \cdot & \cdots & \cdot & \cdots & \cdot \\ \cdot & x & & x & & x \\ \vdots & & & & & \\ \cdot & x & & \xi + \frac{1}{N_i + N_j} & & -\frac{1}{N_i + N_j} \\ \vdots & & & & & \\ \cdot & x & & -\frac{1}{N_i + N_j} & & \eta + \frac{1}{N_i + N_j} \end{vmatrix} \qquad (B.1)$$

The terms $1/(N_i + N_j)$ in the matrix elements arise from the segment connecting elements i and j; the values of ξ and η depend on what other segments end on elements i and j, respectively.

Now let us treat the intermediate element k as a junction, the $(n + 1)^{st}$ in the network. When this is done, the determinant Γ for the network will have a different form. We call this new determinant G. Its lower right corner has the following appearance:

$$G = \begin{vmatrix} \cdot & \cdot & \cdots & \cdot & \cdots & \cdot \\ \cdot & x & x & x & 0 \\ \vdots & & & & \\ \cdot & x & \xi + \frac{1}{N_i} & 0 & -\frac{1}{N_i} \\ \vdots & & & & \\ \cdot & x & 0 & \eta + \frac{1}{N_j} & -\frac{1}{N_j} \\ \vdots & & & & \\ \cdot & 0 & -\frac{1}{N_i} & -\frac{1}{N_j} & \frac{1}{N_i} + \frac{1}{N_j} \end{vmatrix} \qquad (B.2)$$

Junction n - 1 (element i) is no longer connected directly to junction n, but is connected to junction n + 1 by a chain of N_i links-hence the zero in the next to last column, and the entry $-1/N_i$ in the last column of row n - 1. Junction n + 1 (element k) is connected only to junctions n - 1 and n; all elements in the last row and column not shown above are zero.

We now wish to compute the value of η for element k–that is, η_{n+1} when the junctions are numbered as above. Denoting by $G^{kl\ldots}_{ij\ldots}$ the determinant obtained from G by striking out rows i,j,... and columns k, l, ..., and multiplying by $(-1)^{i+j+k+l+\ldots}$, we have, by equation 5.4 of Reference 4,

$$\eta_{n+1} = G^{n+1}_{n+1}/G \qquad (B.3)$$

By adding $N_j/(N_i + N_j)$ times the last column to G to the n - 1^{st} column, and $N_i/(N_i + N_j)$ times the last column to the n^{th} column, one can reduce to 0 the off-diagonal elements in the last row. This same manipulation makes G identical with Γ, except for the presence of the last row and column. It follows at once that:

$$G = \left(\frac{1}{N_i} + \frac{1}{N_j}\right)\Gamma \tag{B.4}$$

We now write G_{n+1}^{n+1} in a form which emphasizes its relation to Γ:

$$G_{n+1}^{n+1} = \begin{vmatrix} \cdot & \cdot & \cdots & \cdot & \cdots & \cdot \\ \cdot & x & & x & & x \\ \cdot & x & & \xi + \dfrac{1}{N_i+N_j} + \alpha & & -\dfrac{1}{N_i+N_j} + \beta \\ \cdot & x & & -\dfrac{1}{N_i+N_j} + \beta & & \eta + \dfrac{1}{N_i+N_j} + \gamma \end{vmatrix} \tag{B.5}$$

where:

$$\alpha = \frac{N_j}{N_i\,(N_i + N_j)}$$

$$\beta = \frac{1}{N_i + N_j} \tag{B.6}$$

$$\gamma = \frac{N_i}{N_j\,(N_i + N_j)}$$

All elements of G_{n+1}^{n+1} not shown above are identical with the corresponding elements in Γ. It is evident that G_{n+1}^{n+1} depends on α, β, γ in the following way:

$$G_{n+1}^{n+1} = K + A\alpha + B\gamma + C\alpha\gamma + D\beta + E\beta^2 \tag{B.7}$$

where K,A,... are independent of α, β, γ. Inspection of the determinant shows that:

$$K = \Gamma \quad A = \Gamma_i^i \quad B = \Gamma_j^j \quad C = \Gamma_{ij}^{ij} \quad D = 2\Gamma_i^j \quad E = -\Gamma_{ij}^{ij} \tag{B.8}$$

The terms in $\alpha\gamma$ and β^2 cancel, and we have:

$$G_{n+1}^{n+1} = \Gamma + \frac{N_j\Gamma_i^i}{N_i(N_i + N_j)} + \frac{N_i\Gamma_j^j}{N_j(N_i + N_j)} + \frac{2\Gamma_i^j}{N_i + N_j} \tag{B.9}$$

Substituting equations B.4 and B.9 into B.3, and, remembering that:

$$\Im_i = \Gamma_i^i/\Gamma \tag{B.10}$$

$$\Im_i + \Im_j - \Im_{ij} = 2\Gamma_i^j/\Gamma \tag{B.11}$$

by equations 5.4 and 7.7 of an earlier paper (4), one obtains:

$$\Im_{n+1} = \frac{N_iN_j}{N_i + N_j}\left\{1 + \frac{\Im_{n-1}}{N_i} + \frac{\Im_n}{N_j} - \frac{\Im_{n,n-1}}{N_i + N_j}\right\} \tag{B.12}$$

This is the same, except for notation, as equation 50.

Acknowledgment

We would like to express our appreciation for support in part of this work by ONR Navy Contract N6-ori-83.

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Synopsis

The approximations implicit in the use of the Gaussian network model for soft rubber are discussed. It is shown that the form of the stress–strain curve can be derived for this model simply, and without special assumptions about the form or behavior of the network. The common assumption that the network junctions are fixed, or can be treated as fixed, is discussed. It is shown that this picture of the situation is unrealistic: the junctions have a Brownian motion comparable to that of any portion of the intervening molecular segments. The introduction of this assumption is not generally admissible, but it will not affect the outcome of certain types of calculation; in particular, one can foresee that it need not affect the calculated form of the stress-strain curve. A particularly simple and straightforward calculation of the network entropy on this basis is given. Wall's theory of rubber is analysed. It is shown that Wall's postulates are not consistent with the network structure of rubber, and in general lead to different results.

Résumé

Les approximations, inclues dans l'utilisation d'un modèle en réseau de Gauss pour le caoutchouc, sont soumises à discussion. L'allure des courbes tension-déformation peut être dérivée de ce modèle simplement, sans préjuger de la forme ou du comportement de ce réseau. En discutant la supposition généralement admise, que les points de jonction du réseau sont fixes ou peuvent être considérés tels, on constate que cette interprétation ne correspond pas à la réalité:les jonctions possèdent un mouvement Brownien comparable à celui de chaque partie des segments moléculaires présents. L'introduction de cette hypothèse n'est pas généralement admissible; certains résultats de calculs toutefois restent inchangés; en particulier, on peut prévoir que la forme calculée de la courbe tension-déformation n'en sera pas affectée. Un calcul particulièrement simple et nouveau

de l'entropie du réseau dans ces conditions est donné. La théorie du caoutchouc de Wall est analysée; ses postulats sont incompatibles avec la structure en réseau du caoutchouc, et amènent en général à des résultats différents.

Zusammenfassung

Es werden die Vernachlässigungen, die sich für die Anwendung der Gausschen Netzwerktheorie auf Weichgummi ergeben, diskutiert. Es wird gezeigt, dass die Gestalt der Zug-Spannungskurve für dieses Modell einfach, und ohne spezielle Voraussetzungen für die Form und das Verhalten der Netzwerke abgeleitet werden kann. Es wird die allgemein übliche Annahme, dass die Knotenpunkte festgelegt sind-oder als festgelegt betrachtet werden können, diskutiert. Es wird gezeigt, dass diese Vorstellung unrealistisch ist. Die Knotenpunkte haben eine Brownsche Bewegung, die der jeden Teiles der sie verbindenden molekularen Segmente vergleichbar ist. Die Einführung dieser Annahme ist nicht allgemein zulässig, aber wenn man est tut, wird das resultat gewisser Berechnungen nicht beeinflusst werden; im besonderen kann man voraussehen, dass die berechnete Form der Zug-Spannungskurve unbeeinflusst bleibt. Auf dieser Grundlage wird eine besonders einfache und elegante Berechnung der Netzwerkentropie gegeben. Walls Gummitheorie wird analysiert. Es wird gezeigt, dass die Postulate dieser Theorie nicht in Einklang mit der Netzwerkstruktur von Kautschuk stehen, und im allgemeinen zu verschiedenen Resultaten führen.

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Ionic Polymerization of Mono-olefinic Hydrocarbons at Low Temperatures. A Review of Proposed Mechanisms

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INTRODUCTION

Although the marked tendency of unsaturated hydrocarbons to polymerize in the presence of Friedel-Crafts type catalysts had been recognized (1) long before 1930, Otto and co-workers (2) were perhaps the first to obtain high polymers in consistent yields from monoolefins at low temperatures. On the other hand, Waterman and co-workers (3) were among the first to publish extensive data resulting from a systematic study of the catalytic action of these electrophilic metal halides in initiating polymer growth at temperatures well below 0°C. Prior and subsequent to this early work, numerous patents were issued claiming semisolid products from branched-chain olefins at temperatures below -10°C. in the presence of aluminium chloride (4). In addition, considerable work has been done in the preparation of synthetic lubricating oils from unsaturated hydrocarbons in the presence of similar catalysts and at temperatures in the neighborhood of 0°C. and above (5). While Waterman and his associates (6-8) continued to publish the results of their systematic investigations through 1939, the most significant advances in techniques and practices in the low-temperature field of polymerization were evidenced in patents issued to Otto and Mueller-Cunradi, Howard, Frolich, Zimmer, Carlson, and Schneider (9). Subsequently, Thomas, Sparks, and Frolich (10-12) published the results of their extensive work on the homopolymerization of isobutylene and its copolymerization with butadiene and isoprene in the presence of boron trifluoride and similar electrophilic catalysts. Since the advent of butyl rubber, numerous patents have been issued covering many types of hydrocarbon polymers and copolymers prepared from a variety of olefins, diolefins, their derivatives, and combinations of the same.

More recently, Evans, Polanyi, Plesch, Skinner, Norrish, Houtman, Pepper, and others have published results of numerous fundamental studies in this field (13-29).

GENERAL CONCEPTS

There is general agreement among the various investigators that the metal halide-catalyzed polymerization of unsaturated hydrocarbons at low temperature involves an ionic mechanism. In addition to the well-known works of Hunter and Yole (30) and Whitemore (31) Hulbert, Harman, Tobolsky, and Eyring (32) have discussed, in some detail, the ionic mechanism of polymerization and cite the criteria of an ionic or polar reaction. One of the criteria, acid catalysis, is of immediate interest to the present discussion. Aluminum chloride, boron fluoride, and sulfuric acid are classified as catalysts capable of forming a bond with any molecule capable of furnishing a pair of electrons. That is, the ability of metal halide catalysts to initiate the polymerization of unsaturated hydrocarbons depends upon the bonding effect of the catalyst for the unsaturation or pi electron pair. Thus, in the presence of the catalyst, polarization of the unsaturate takes place with the formation of a dipole and the electron pair is stabilized on one carbon atom. With regard to the relative catalytic power of some of the common Friedel-Crafts salts, the following sequence has been observed, in order of decreasing activity and acid strength: BF_3, $AlBr_3$, $TiCl_4$, $TiBr_4$, BCl_3, BBr_3, and $SnCl_4$ (20). Thus, electrophilic salts such as BF_3, and $AlBr_3$, induce polarization of the unsaturate more readily than, for instance, $SnCl_4$.

Two other general criteria of an ionic reaction — the change in rate upon changing the electronegativity of the substituents, and intramolecular rearrangements — are satisfied by observations made in the polymerization of unsaturated hydrocarbons in the presence of Friedel-Crafts type catalysts. The former is strikingly illustrated in comparisons involving the homopolymerizing tendencies of such monomers as ethylene, propylene, isobutylene, 1- and 2-butene, styrene, and alpha-methylstyrene. Price (33) has suggested that it is perhaps significant that those substances most readily polymerized possess substituents such as alkyl, aryl, or ether groups, which tend to promote the release of electrons. It follows, therefore, that monomers such as the acrylates which possess groups exhibiting marked electronegativity do not readily respond to acid catalysis (34). It is evident, then, that for a given catalyst, the reactivities of the various monomers will depend, primarily, upon the ease of displacement of the electron pair—a prerequisite to dipole formation. It has been suggested (28) that the marked reactivity of isobutylene is due, at least in part, to the fact that the free electron pair is already polarized to a certain extent. Thus, the pi electron pair will be more readily fixed by the electrophilic salt. On the other hand, the pi electron pair of ethylene is evidently much more resistant to polarization, and this is attested, at least qualitatively, by the fact that ethylene evidences no tendency to polymerize in the presence of metal halide catalysts at low temperatures. While isobutylene is quite reactive, its dimer, diisobutylene is quite sluggish (10, 17, 18) which may result, in part, from the fact that the pi electron pair is considerably less polarized. In addition, it has been indicated (14, 28) that extensive growth of the latter cannot take place because of steric hindrance offered by large side groups.

While intramolecular rearrangements may play a prominent role in acid-catalyzed polymerizations at temperatures above 0°C. (31), little information is available to indicate whether this phenomenon functions to any degree in reactions conducted at temperatures well below 0°C. Waterman (7) has indicated that ring structures are present in polymers prepared from isobutylene at -45°C. However, spectroscopic and other data on polyisobutylenes prepared at temperatures in the neighborhood of -100°C. indicate a striking regularity of structure (10, 35, 36). It is possible, theoretically at least, that the termination step might involve some form of intramolecular rearrangement. However, an examination of the mechanisms will indicate that cessation of growth and establishment of terminal unsaturation may be accomplished by transformations excluding rearrangements of any pronounced magnitude.

In light of the above, it is reasonable to assume that an ionic mechanism functions in the metal halide catalyzed polymerizations of unsaturated hydrocarbons at low temperatures and that the reaction may be initiated, propagated, and terminated by an ionic mechanism. It has been suggested (32) that the true configuration of the unsaturate in the activated state is in all probability largely polar, though not completely ionic, since homopolar states contribute somewhat to the resonance structure.

MECHANISMS

In the ensuing discussion, the following mechanisms will be presented and commented upon.

(1) Dipolar: (a) direct union of the electrophilic metal halide and the unsaturated hydrocarbon to form an organometallic complex intermediate, and (b) thermal activation in the presence of a metal halide and a third component capable of reacting with it to produce energy (exothermic heat) necessary for internal ionization (dipole formation).

(2) Carbonium ion: (a) addition of hydrogen halide and other acids to metal halides and subsequent ionization of the complex to furnish protons, a requisite for carbonium ion formation and (b) addition of water to metal halide to produce a hydrate acid which, in turn, may furnish protons with resultant carbonium ion formation.

(3) Dehydrohalogenation: catalyzed addition of hydrogen halide to the unsaturate in the presence of an electrophilic metal halide, and subsequent dehydrohalogenation involving alkyl halide and unsaturate.

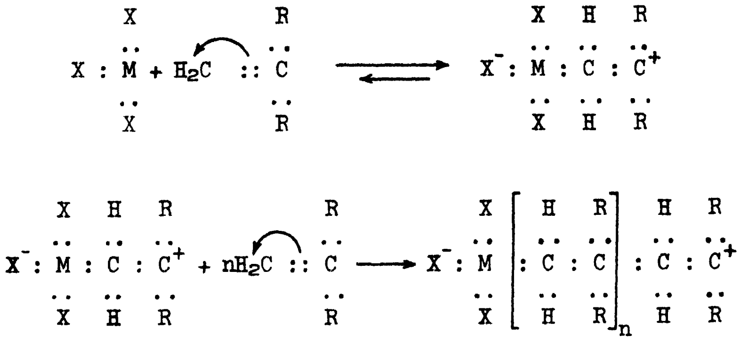
Dipolar Mechanism

Organometallic Complex

This mechanism, proposed by Hunter and Yohe (30) and others, involves the direct addition of metal halide to the unsaturated hydrocarbon — that is, the electron-deficient nature of the electrophilic salt and resultant ease of association with a pair of electrons of the polarized unsaturate are emphasized. Whitmore (37) has given the name "heterocarbonium ion" to this organometallic complex in order to distinguish it from the "true" carbonium ion which is formed by the union of the unsaturate and a proton. He indicates that the former is quite stable and, therefore, considerably less reversible than the latter. Some degree of reversibility in the initial association of catalyst and monomer is indicated by the work of Williams (38), who found that in the polymerization of styrene in carbon tetrachloride with stannic chloride the rate was dependent on an order higher than third with respect to monomer concentration.

The equations, which follow, outline the reaction mechanism and suggest several possibilities with regard to the termination step.

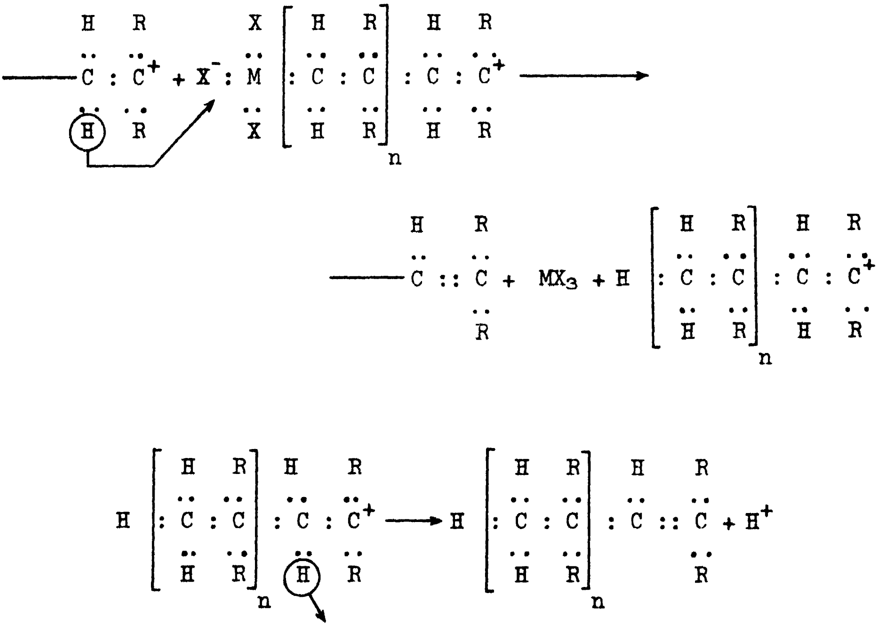
Initiation and Propagation.



where MX_3 is an electrophilic metal halide (e.g., BF_3 or $AlCl_3$).

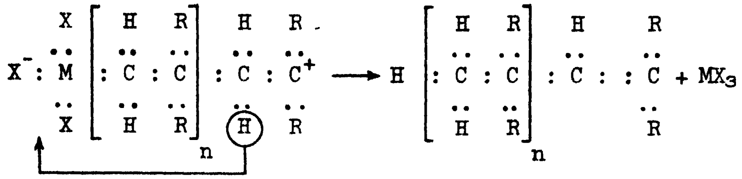
Termination. Cessation of growth may occur, perhaps, through a reaction characterized by one or more of the following equations.

(a) The cationic or growing end of the chain may collide with the anionic or "metal halide end" of another chain, resulting in the establishment of terminal unsaturation in both chains and release of a single proton:



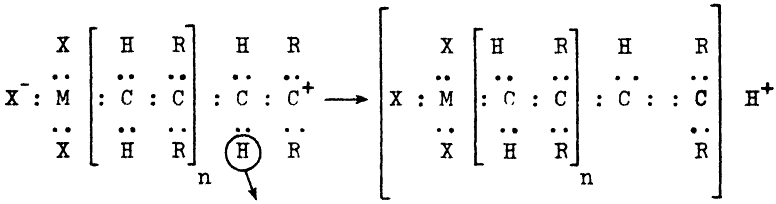
Bimolecular termination is indicated while the work of Williams (37) indicates that the cessation step is a unimolecular one. In addition, it is questionable whether metal halide may be regenerated in this manner in light of the known difficulties of separating residual catalyst from the polymeric product (39).

(b) A proton may shift from the carbon atom alpha to the "carbonium carbon" to the anionic or "initiation end" of the chain with simultaneous elimination of metal halide:

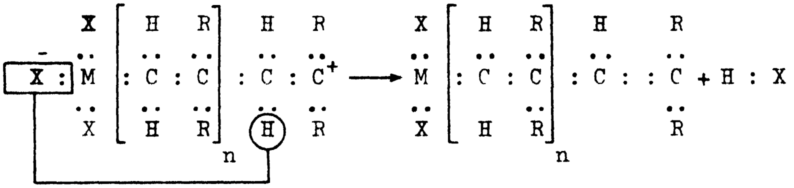


Although this mechanism indicates a unimolecular termination, it is rather improbable that an intramolecular transformation of this magnitude takes place at the reaction conditions employed.

(c) A proton may be lost from the growing or cationic end of the chain. This would result in the formation of terminal unsaturation and might be considered a logical inference from Price's outline (33) of the mechanism. Although this might be considered to be a modification of the Whitmore mechanism (31), the simple loss of a proton will not produce a neutral, stable compound.



(d) Marvel and Hornung (40) have proposed a chain-termination step involving the loss of (1) a proton from the cationic or growing end of the chain and (2) a chloride ion from the anionic or opposite end:



A mechanism involving the elimination of hydrogen halide is open to question in light of the known retarding effects of the halide. However, the possibility of HX elimination in the termination step may, perhaps, offer an explanation of the observed slowing down of the reaction rate in mixtures which have been extensively treated with catalyst.

In light of the known enhancing effects of small amounts of water and/or hydrogen halide in other Friedel-Crafts catalyzed transformations such as alkylation and isomerization, it was suggested a number of years ago (41) that, in all probability, the electrophilic salt, per se, is not responsible for the pronounced activation of unsaturated hydrocarbons at low temperatures. Hydrogen halide, held to be present in Friedel-Crafts catalysts despite rigorous purification, was suggested as a so-called third component. The presently discussed mechanism, employing the electrophilic salt as the sole activator—was further criticized not only on the grounds that it necessitated correlating complex formation with activity, but that many of the complexes were found to be too stable to promote reaction.

Recent investigations (16, 20) have supported, to some degree, the aforementioned idea that the electrophilic salt, per se, is incapable of initiating extensive polymerization at low temperatures. Mechanisms involving acids and water as third components will be discussed under "Carbonium Ion Mechanisms," since their introduction into the initiation step necessitates giving consideration to an over-all proton concept rather than the "dipolar or heterocarbonium" type.

While recent investigations tend to stress the necessity of a so-called third component and the dominant role of the proton, there are several well-established points which give credence to the existence of some form of organometallic intermediate: (a) numerous organometallic complexes resulting from the union of electrophilic metal halides and unsaturates are known to exist and some have been isolated as chemical entities; and (b) it has long been known (39) that it is practically impossible to separate polymeric material from residual catalyst without resorting to the use of compounds possessing active hydrogen, such as alcohols and ammonia which readily sever organometallic bonds.

Houtman, in a recent article (28), expresses the view that high-molecular products are obtained when the halide itself takes part in reaction, and not the hydrate or acid that may be formed by inclusion of the so-called third component. He suggests, furthermore, that in certain cases steric hindrance may be present in monomer and/or catalyst, and that this factor may play an important role in determining the reactivity of various monomer-catalyst systems.

Despite Houtman's objections, recent work (16, 18, 20) has indicated that a purely dipolar mechanism involving an organometallic intermediate is inadequate and does not explain observed phenomena satisfactorily. However, one should not deduce from this that organometallic complex formation cannot take place and that we may explain all observations satisfactorily in terms of a purely proton-activated system. It will suffice to mention at this point that organometallic complex formation may perhaps take place in systems involving a third component, and that such a mechanism would involve a negative ion complex rather than a dipolar one.

Thermal Activation

A second possibility exists with regard to a purely dipole type of mechanism, namely, that of thermal activation. If one concurs with the idea that a third component is a necessary prerequisite for initiation, then, theoretically at least, the initiation step may perhaps be realized through energy supplied by the reaction of an electrophilic salt with an acid or water. A purely thermal mechanism of this type has been commented upon by Evans et al. (16) insofar as it would be in agreement with observations made regarding the effect of the third component. That is, an energy chain mechanism would be in agreement with the idea that once the so-called third component has participated it cannot do so a second time. However, it may be added that a "carbonium ion mechanism" would also be in agreement with this idea.

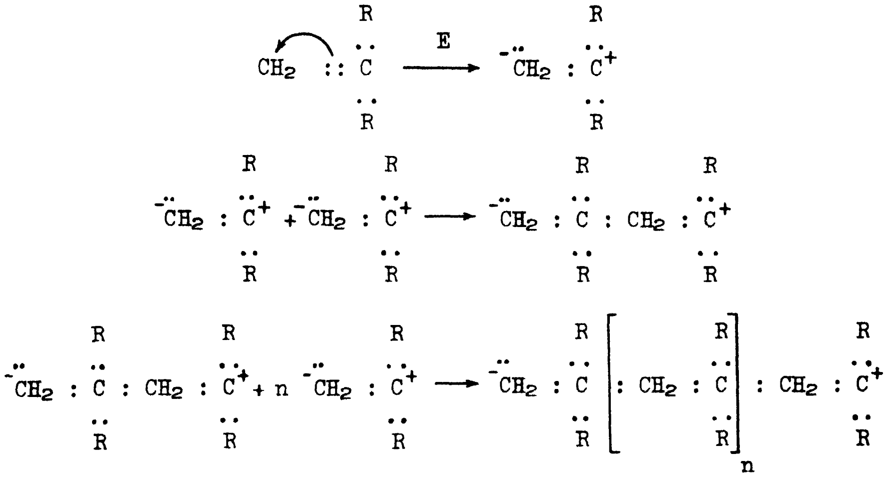
In a thermal activation, the energy (exothermic heat) supplied by reaction of the metal halide and the third component would polarize the unsaturate with resultant dipole formation. The principal steps involved might be pictured as follows:

$$MX_n + HA \longrightarrow MX_n{\cdot}HA + E$$

$$MX_n + HOH \longrightarrow MX_n{\cdot}OH_2 + E$$

where E = energy from exothermic heat of reaction, and n = 3 or 4.

Initiation and Propagation.

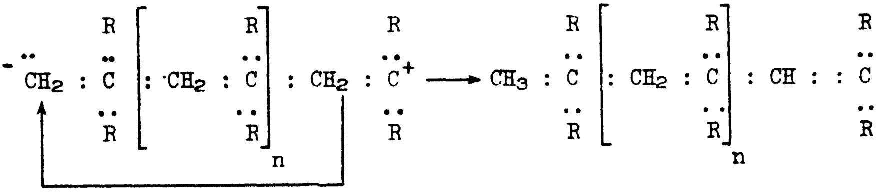


$$CH_2 :: \overset{R}{\underset{R}{C}} \xrightarrow{E} {}^{-}CH_2 : \overset{R}{\underset{R}{C^+}}$$

$${}^{-}CH_2 : \overset{R}{\underset{R}{C^+}} + {}^{-}CH_2 : \overset{R}{\underset{R}{C^+}} \longrightarrow {}^{-}CH_2 : \overset{R}{\underset{R}{C}} : CH_2 : \overset{R}{\underset{R}{C^+}}$$

$${}^{-}CH_2 : \overset{R}{\underset{R}{C}} : CH_2 : \overset{R}{\underset{R}{C^+}} + n\,{}^{-}CH_2 : \overset{R}{\underset{R}{C^+}} \longrightarrow {}^{-}CH_2 : \overset{R}{\underset{R}{C}} \left[: CH_2 : \overset{R}{\underset{R}{C}} \right]_n : CH_2 : \overset{R}{\underset{R}{C^+}}$$

Cessation.



$${}^{-}CH_2 : \overset{R}{\underset{R}{C}} \left[: CH_2 : \overset{R}{\underset{R}{C}} \right]_n : CH_2 : \overset{R}{\underset{R}{C^+}} \longrightarrow CH_3 : \overset{R}{\underset{R}{C}} \left[: CH_2 : \overset{R}{\underset{R}{C}} \right]_n : CH :: \overset{R}{\underset{R}{C}}$$

In light of known facts regarding metal halide catalyzed polymerization of unsaturated hydrocarbons at low temperatures, this mechanism is highly improbable and merits no serious consideration. Thus, from observations regarding the strong affinity that electrophilic metal halides have for unsaturates, and the marked difficulty of removing catalyst from polymeric products, it is not likely that the unsaturate and the catalyst will remain as distinct entities in an intimate mixture. Even if organometallic complex formation were precluded as a possibility, the proton, presumably generated in a third-component system by reaction of metal halide with acid or water, would be capable of inducing polarization with resultant carbonium ion formation.

Carbonium Ion Mechanism

Acid Cocatalyst

As previously mentioned, exception has been taken to considering the electrophilic salt, per se, as the activator (41). The extreme difficulty and alleged impossibility of freeing typical Friedel-Crafts catalysts of small amounts of attendant hydrogen halide has led to the suggestion that in all probability the hydrogen halide present as a third component actively participates in the initiation and that a mechanism neglecting the same does not present a true picture of the pertinent factors involved.

Thus, the existence of an addition compound of metal halide and hydrogen halide is postulated, which may be considered to be a relatively strong acid. This may subsequently ionize to furnish a proton that is capable of adding to an unsaturated hydrocarbon to form a carbonium ion. The intermediate would be similar to that postulated by Whitmore (31), and may either stabilize itself by the ejection of a proton and simultaneous regeneration of unsaturation, or may react with another molecule of unsaturate to form a carbonium ion of higher molecular weight. The following equations indicate the possible reactions involved:

$$HX + MX_n \longrightarrow HMX_{n+1}$$

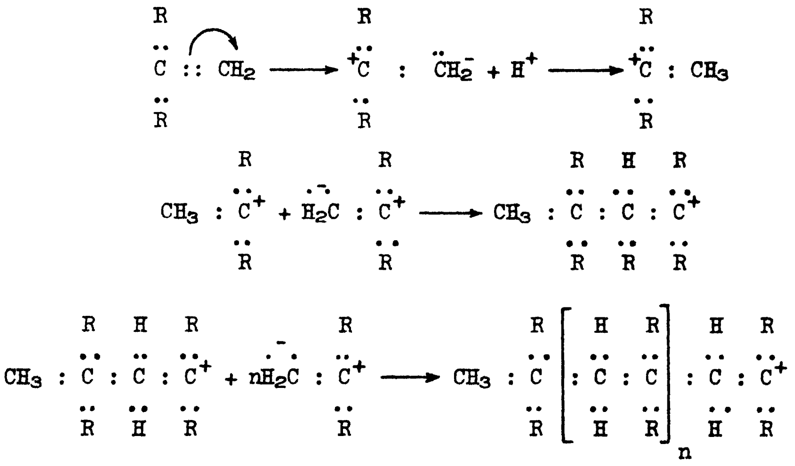
$$HMX_{n+1} \longleftrightarrow H^+ + MX^-_{n+1}$$

Or, in the general case:

$$HA + MX_n \longrightarrow MX_n \cdot HA$$

$$MX_n \cdot HA \longleftrightarrow H^+ + MX_n \cdot A^-$$

Initiation and Propagation.

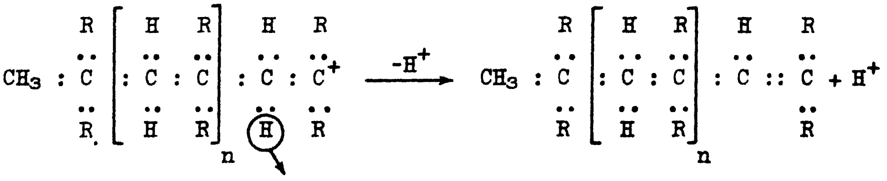


$$\overset{R}{\underset{R}{C}} :: CH_2 \longrightarrow {}^{+}\overset{R}{\underset{R}{C}} : CH_2^{-} + H^+ \longrightarrow {}^{+}\overset{R}{\underset{R}{C}} : CH_3$$

$$CH_3 : \overset{R}{\underset{R}{C}}{}^{+} + H_2C : \overset{R}{\underset{R}{C}}{}^{+} \longrightarrow CH_3 : \overset{R}{\underset{R}{C}} : \overset{H}{\underset{R}{C}} : \overset{R}{\underset{R}{C}}{}^{+}$$

$$CH_3 : \overset{R}{\underset{R}{C}} : \overset{H}{\underset{H}{C}} : \overset{R}{\underset{R}{C}}{}^{+} + nH_2C : \overset{R}{\underset{R}{C}}{}^{+} \longrightarrow CH_3 : \overset{R}{\underset{R}{C}} \left[: \overset{H}{\underset{H}{C}} : \overset{R}{\underset{R}{C}} \right]_n : \overset{H}{\underset{H}{C}} : \overset{R}{\underset{R}{C}}{}^{+}$$

Termination. Termination of chain growth may occur through the ejection of a proton and the simultaneous establishment of terminal unsaturation:



$$CH_3 : \overset{R}{\underset{R}{C}} \left[: \overset{H}{\underset{H}{C}} : \overset{R}{\underset{R}{C}} \right]_n : \overset{H}{\underset{\textcircled{H}}{C}} : \overset{R}{\underset{R}{C}}{}^{+} \xrightarrow{-H^+} CH_3 : \overset{R}{\underset{R}{C}} \left[: \overset{H}{\underset{H}{C}} : \overset{R}{\underset{R}{C}} \right]_n : \overset{H}{C} :: \overset{R}{\underset{R}{C}} + H^+$$

While Waterman (7) has indicated that the addition of gaseous hydrogen chloride aided materially in the polymerization of a refractory monomer such as cyclohexene, other investigators have noted the pronounced poisoning effects of hydrogen halides and have classified them as active chain breakers (10,38,42). Plesch and co-workers (20) in studying the effect of various cocatalysts have reported that added hydrogen chloride does not enhance the polymerization of isobutylene in the condensed phase.

Although the proton, per se, is credited in this mechanism with being the active component in the initiation step, it may be pointed out that neither hydrogen chloride nor hydrogen fluoride is capable of activating normally gaseous olefins at temperatures well below 0^oC. It has been found that concentrated sulfuric acid induces extensive growth of styrene and alpha-methylstyrene at temperatures in the neighborhood of -50^oC. but has no effect on monomers such as propylene and isobutylene (43). Plesch has indicated in a recent article (26) that concentrated sulfuric acid and oleum, in the absence of metal halide, have no effect on isobutylene at temperatures in the range of -80^oC. On the other hand, acids such as acetic, trichloroacetic, and sulfuric were found under certain conditions to be effective cocatalysts for the polymerization of isobutylene (26). The choice of acid as cocatalyst appears to be rather critical and no generalizations are as yet in order. For instance, two acids may possess similar dissociation constants and yet differ markedly in their ability to induce polymerization when employed as a cocatalyst with the metal halide. Thus, trichloroacetic and picric acids possess similar dissociation constants. However, the former, when added to an $i\text{-}C_4H_8$ - $TiCl_4$ system in hexane, readily initiated the reaction while the latter was found to be inactive (26).

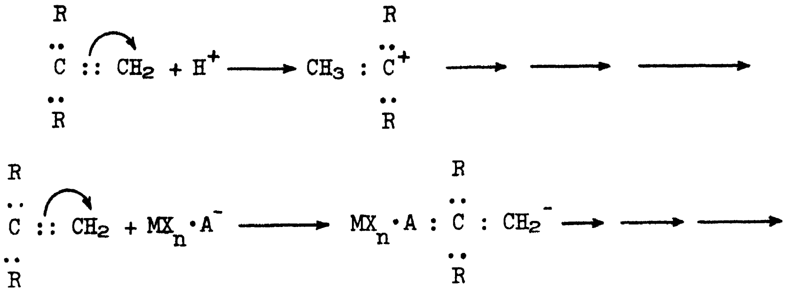
It would appear that if we give credence to a mechanism involving an acid as the third component (cocatalyst), the critical step would be that of the dissociation of the complex to furnish protons in sufficient concentration to induce polarization of the unsaturate. Stress should be placed on the degree of dissociation of the complex and not of the acid, per se. This may, perhaps, explain the ineffectiveness of mineral acids in the absence of metal halide, at temperatures well below 0^oC. That is, although appreciable solution may be realized, the requisite proton concentration is not made available, due to limited dissociation.

The complexity involved in systems employing acid cocatalysts is illustrated in a recent report by Plesch (26) which indicated that acetic acid, an effective cocatalyst in the boron trifluoride catalyzed, room-temperature, gas-phase polymerization of isobutylene, functioned as an inhibitor in a low-temperature, liquid-phase (hexane) polymerization of the same monomer employing titanium tetrachloride. The cocatalyst was appreciably soluble in the diluent. Again, it may well be that the complex did not dissociate sufficiently in hexane at the temperature employed to yield the requisite concentration of of protons for initiation.

As previously noted, proposals involving an acid cocatalyst have suggested a relatively simple proton type of activation with resultant carbonium ion formation. However, in light of observations regarding the difficulty of removing residual catalyst from polymeric products without resorting to reagents capable of splitting organometallic bonds, it appears rather probable that the metallic halide in one form or another intimately associates with the unsaturate and takes part in the initiation step. It is possible, therefore, that a dual initiation mechanism may function, in which both cation and anion may be capable of activating growth. Thus:

$$MX_n + HA \longrightarrow MX_n\cdot HA$$

$$MX_n\cdot HA \longleftrightarrow H^+ + MX_n\cdot A^-$$



$$\overset{R}{\underset{R}{\ddot{\underset{\cdot\cdot}{C}}}}::CH_2 + H^+ \longrightarrow CH_3:\overset{R}{\underset{R}{\ddot{\underset{\cdot\cdot}{C}}}}{}^+ \longrightarrow \longrightarrow \longrightarrow$$

$$\overset{R}{\underset{R}{\ddot{\underset{\cdot\cdot}{C}}}}::CH_2 + MX_n\cdot A^- \longrightarrow MX_n\cdot A:\overset{R}{\underset{R}{\ddot{\underset{\cdot\cdot}{C}}}}:CH_2^- \longrightarrow \longrightarrow \longrightarrow$$

A bimolecular cessation might occur as a result of collision between positive and negative chains whose growth was initiated by cation and anion, respectively. However, this would be at variance with the findings of Williams (38) which indicated a unimolecular termination. While terminal unsaturation is not likely to be generated by the coupling of two oppositely charged chains, a bimolecular termination involving proton transfer would confer terminal unsaturation upon the chain whose growth was initiated by the proton. A dual mechanism of this type has been suggested by Norrish et al. (23) in cases in which water constitutes the cocatalyst. Such a proposal has not been substantiated in any way. However, it does suggest a possible explanation for the catalyst residues invariably associated with polymeric products.

The concept of an acid cocatalyst combining with a metal halide to form a complex which subsequently ionizes to furnish the protons necessary for activation presents complications which challenge experimental verification. If we accept the premise that the cocatalyst is a prerequisite for activation, it will be necessary to account for the apparent variations reported to date (28) and the marked speciificities exhibited by various combinations of metal halides and cocatalysts (26). While isobutylene has shown little tendency to polymerize in the gaseous phase when catalyzed by boron trifluoride in the absence of a cocatalyst, no similar lack of reactivity is evidenced in the liquid phase, where, despite rigorous purifications, activation is readily accomplished. On the other hand, titanium tetrachloride, in the absence of a cocatalyst, will not activate the same monomer in the liquid phase (16, 20). If we confine ourselves to the liquid phase and the aforementioned catalysts, the possibility arises that with an extremely active metal halide such as boron trifluoride, little cocatalyst is required. In fact, the amount of cocatalyst generated in situ in a condensed system at low temperature, regardless of pretreatment of reactants, and although incapable of being accurately determined, may be sufficient to give the requisite proton concentration. Since boron trifluoride is among the most active of Friedel-Crafts catalysts, it follows that the amount of cocatalyst required to initiate growth through complex formation with this metal halide will be less than that required when employing a less reactive member such as titanium tetrachloride. In terms of the proton concept, the former will require less cocatalyst to give an equivalent proton concentration.

Little data are available that might permit a comparison of gas- and liquid-phase polymerizations. Houtman (28), for instance, has claimed that polymer is obtained from isobutylene-boron trifluoride in either phase despite rigorous precautions. He readily admits, however, that traces of a third component may well have been present. The elimination of traces of cocatalyst from condensed systems is extremely difficult, if not impossible, and the generation in situ of small amounts of the same is apparently sufficient to activate an extremely reactive monomer like isobutylene. It has been suggested (27) that the gas-phase polymerization involving an acid cocatalyst may be a heterogeneous process in which growth is initiated on the highly specific surface of the catalyst complex. In addition, Plesch (26) has noted that the initiation step in the condensed phase may perhaps be heterogeneous in the case where water vapor is the cocatalyst in the isobutylene - titanium tetrachloride system employing hexane as the diluent. The resulting polymer solution was indicated as being milky in appearance. However, in cases in which an acid cocatalyst had been added, no opalescence was observed (26). While insufficient data are available to permit evaluation of the homogeneity or heterogeneity of the process in the liquid phase, there is little reason to believe that the two reactions differ essentially in any manner. In the former case, the introduction of water may well have enhanced the hydrolysis of the catalyst and so reduced its solubility in the hydrocarbon phase. In the latter case, the particular complex of acid and/or metal halide tended to remain in "true" solution. There are apparently no significant data which indicate a heterogeneous process functioning in the condensed phase.

Irregularities noted in recent investigations with regard to conditions necessary for activation may be due, at least in part, to failure of investigators to standardize purification procedures involving monomer, catalyst, and cocatalyst. Since reactive monomers like isobutylene are quite sensitive to small amounts of acid, water, alcohol, etc., reaction mixtures whose constituents have been purified by various methods tend to exhibit widely divergent activity. In a recent study, Norrish (23) has noted the marked effect of rigorous purification.

In summary, it may be remarked that in certain rather specific cases acid cocatalysts when used in conjunction with electrophilic metal halides, appear to enhance materially the polymerization of a reactive, normally gaseous, olefin such as isobutylene. Results obtained in the gaseous phase, at least with isobutylene, are in marked contrast to those obtained in the condensed phase. Little is known with regard to the relative strengths of complexes formed between metal halide and acid and whether these function in the capacity of furnishing protons. The most rigorous purification techniques practiced to date have failed to prevent the liquid phase polymerization of isobutylene in the presence of boron trifluoride.

A mechanism, therefore, involving an acid cocatalyst, while remedying somewhat the shortcomings evidenced by the previous proposal involving direct organometallic complex formation between metal halide and unsaturate, still possesses evident weaknesses which militate against its acceptance as a satisfactory explanation of the general phenomena observed in Friedel-Crafts catalyzed, low-temperature polymerization.

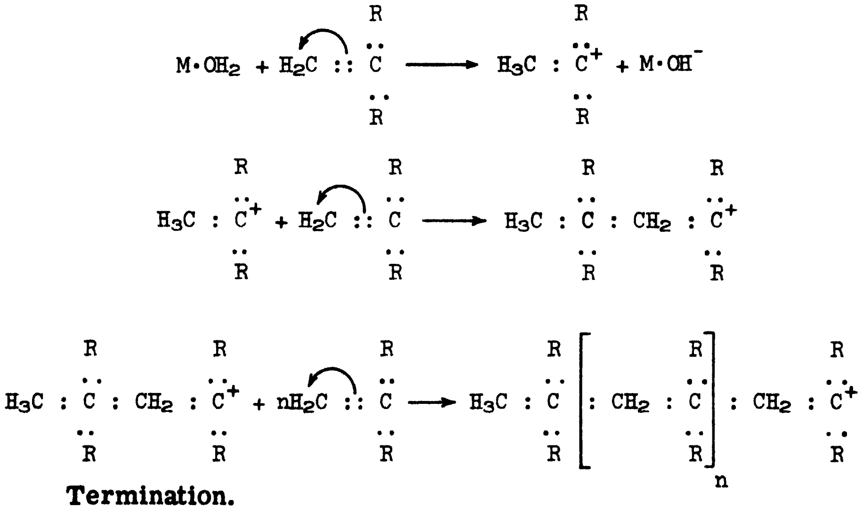
Water As Cocatalyst

Recent investigations in the field of metal halide-catalyzed, low-temperature polymerization have indicated that water, introduced into the reaction mixture in the form of a vapor or in a highly dispersed state, is a necessary prerequisite for polymer formation in the following cases: (a) when reacting isobutylene in the gas phase and diisobutylene in the liquid phase with boron trifluoride (17,18), (b) when reacting isobutylene in the liquid phase with stannic chloride (23) and (c) when reacting isobutylene in the liquid phase with titanium tetrachloride (16,20). It is postulated that a hydrate is formed by the combination of water and the electrophilic metal halide and that the acid complex then loses a proton to the unsaturate with resultant carbonium ion formation. The following equations indicate the series of reactions that may be involved:

$$M + H_2O \longrightarrow M\cdot OH_2$$

where M = BF_3, $TiCl_4$, etc.

Initiation and Propagation.

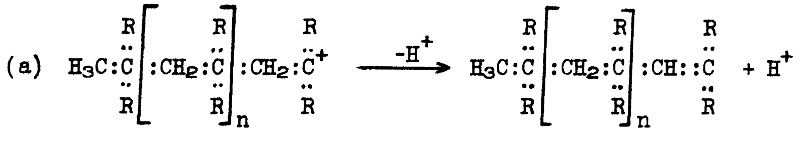


$$M\cdot OH_2 + H_2C::\overset{R}{\underset{R}{C}} \longrightarrow H_3C:\overset{R}{\underset{R}{C^+}} + M\cdot OH^-$$

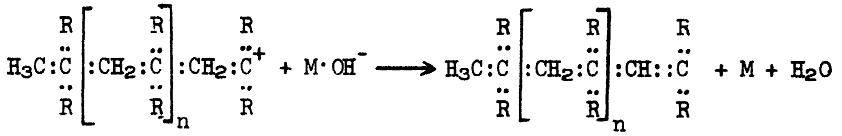
$$H_3C:\overset{R}{\underset{R}{C^+}} + H_2C::\overset{R}{\underset{R}{C}} \longrightarrow H_3C:\overset{R}{\underset{R}{C}}:CH_2:\overset{R}{\underset{R}{C^+}}$$

$$H_3C:\overset{R}{\underset{R}{C}}:CH_2:\overset{R}{\underset{R}{C^+}} + nH_2C::\overset{R}{\underset{R}{C}} \longrightarrow H_3C:\overset{R}{\underset{R}{C}}\left[:CH_2:\overset{R}{\underset{R}{C}}\right]_n:CH_2:\overset{R}{\underset{R}{C^+}}$$

Termination.



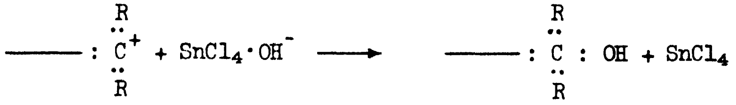
$$(a)\quad H_3C:\overset{R}{\underset{R}{C}}\left[:CH_2:\overset{R}{\underset{R}{C}}\right]_n:CH_2:\overset{R}{\underset{R}{C^+}} \xrightarrow{-H^+} H_3C:\overset{R}{\underset{R}{C}}\left[:CH_2:\overset{R}{\underset{R}{C}}\right]_n:CH::\overset{R}{\underset{R}{C}} + H^+$$

(b) 

$$H_3C{:}\overset{R}{\underset{R}{C}}\left[{:}CH_2{:}\overset{R}{\underset{R}{C}}\right]_n{:}CH_2{:}\overset{R}{\underset{R}{C^+}} + M\cdot OH^- \longrightarrow H_3C{:}\overset{R}{\underset{R}{C}}\left[{:}CH_2{:}\overset{R}{\underset{R}{C}}\right]_n{:}CH{::}\overset{R}{\underset{R}{C}} + M + H_2O$$

It has been observed that the stronger the electrophilic metal halide, the higher is the molecular weight. Termination (b) would be in accord with this since the stronger metal halides would give rise to stronger addition products of the halides with the cocatalyst and the resultant conjugate base would be correspondingly weaker. It follows, therefore, that the weaker the conjugate base, the less likely will be the termination. In addition, recent studies (29) involving the use of solvents have indicated that the molecular weight increases with increasing dielectric constant of the solvent. Termination (b) would be in accord with this observation.

Recent investigations (44) involving the polymerization of isobutylene in ethyl chloride at -90 to -40°C. employing stannic chloride and water as cocatalyst have indicated that the growing chain (carbonium ion) is terminated by a hydroxyl group that is generated by collision of the chain with the conjugate base:



$$\text{———}{:}\overset{R}{\underset{R}{C^+}} + SnCl_4\cdot OH^- \longrightarrow \text{———}{:}\overset{R}{\underset{R}{C}}{:}OH + SnCl_4$$

Hydroxyl groups were reported as constituting an integral part of the chain, thus giving rise to a saturated product. While terminal unsaturation is difficult to determine in products of high molecular weight, its presence has readily been shown to exist in polymers prepared in the absence of added water and possessing lower degrees of polymerization (e.g., polypropylene) (43). It is rather inconceivable that in the absence of added water there would be sufficient hydroxyl groups to effectively terminate the growing chains. It may well be, therefore, that increasing amounts of water in the reaction mixtures affect terminations that result in products evidencing increased hydroxyl content and, thus, increased degrees of saturation.

As previously indicated, Houtman (28) has taken exception to the observations of Evans, Polanyi, and others regarding the necessity of water in metal halide catalyzed, low-temperature polymerization of unsaturated hydrocarbons. However, Evans and associates, in a publication subsequent to the comments of Houtman, have shown rather conclusively that, at least in the gas phase, the polymerization of isobutylene in the presence of boron trifluoride does not take place in absence of a cocatalyst (17,18). This, however, has not been found to be the case in a liquid-phase reaction involving the same monomer and catalyst.

It has been suggested (28) that perhaps two distinct mechanisms may function in these low-temperature polymerizations. One type, involving an organometallic complex would function in the absence of water (dipolar mechanism), and the other, functioning in the presence of water, would involve a proton type of activation (carbonium ion).

It was further remarked that high molecular products would be associated with the former and that products of considerably lower molecular weight would result from the latter. While it is generally recognized that increasing amounts of water result in correspondingly lower molecular weights, no investigator has indicated with certainity that a given electrophilic salt is free of moisture and/or hydrogen halide. It is incorrect, therefore, to associate the presence of a third component with low-molecular products since a basis for comparison is lacking.

The general discussion presented previously for the acid cocatalyst may well be adapted to the presently discussed mechanism involving water as the third component or cocatalyst. That is, a proton initiation (carbonium ion) is postulated upon addition of either water or acid to the metal halide-unsaturate system, and since water is capable of affecting, to a degree, the hydrolysis of the metal halide with formation of acid, there should be no essential difference in the mechanisms involved in reactions catalyzed by the addition of (a) an acid, and (b) water to the system.

It has been suggested (21) that the enhancing effect that Polanyi attributes to hydrate formation in the system, $TiCl_4{-}H_2O{-}(i{-}C_4H_8)$, may possibly be due to hydrogen chloride generated by hydrolysis of titanium tetrachloride in the presence of the water. Hickenbottom (14), commenting on the presence of a third component, refers to similar observations made by Ipatieff and associates (36) in connection with olefin reactions such as polymerization and alkylation. He suggets that, if hydrogen halide is the cocatalyst, then it is quite possible that the olefin acts as a proton acceptor and that the function of the catalyst is to cause reaction between a charged olefin addendum and another monomeric unit.

On the other hand, Plesch (20) has indicated that anhydrous hydrogen chloride evidenced no activating effect when added at low temperature to a condensed system containing isobutylene and a metal halide catalyst. However, the effect produced when hydrogen halide is added to the metal halide—unsaturate system may perhaps be quite different than that obtained when the acid is generated in situ. Alkyl halides may be prepared by addition of hydrogen halide to unsaturates at low temperature in the presence of metal halides (45). Thus, the added hydrogen halide may be taken up immediately by the double bond and therefore exhibit no activating effect directed toward polymer growth. Or it may be that an active complex cannot stem from anhydrous hydrogen halide and a metal salt.

On the other hand, the small amount of acid generated in situ through the action of moisture on the metal halide may immediately associate itself with the salt and thus give rise to the active complex responsible for initiation:

$$MX_n + HOH \longrightarrow MX_{n-1}\,OH \cdot HX$$

$$MX_{n-1}OH \cdot HX \longleftrightarrow MX_nOH^- + H^+$$

Those acids found to be active cocatalysts upon addition to the reaction mixture would in all probability show little tendency to add to the double bond under the reaction conditions employed, complex formation with the metal halide being preferred. It has been pointed out (26) that acids differ markedly in their ability to enter into complex formation with a metal halide.

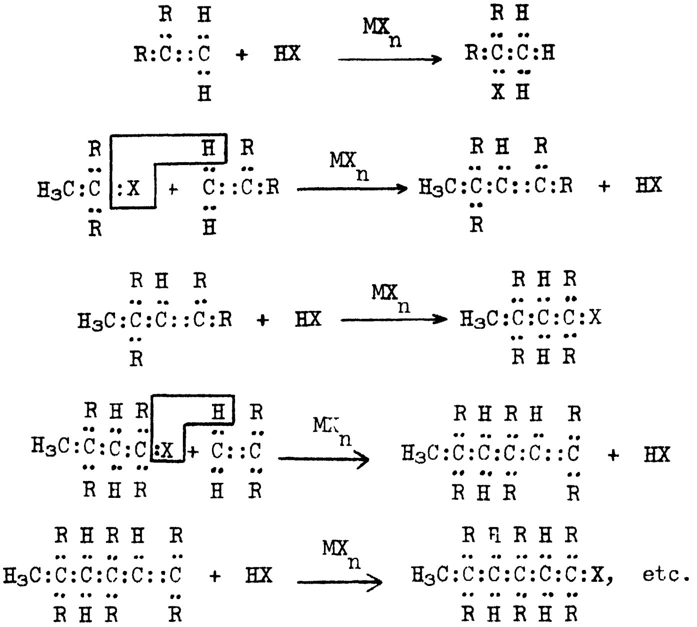
It may be remarked, in summary, that the anomalies and variable results that have appeared in reported data may well stem from the fact that standards of purity for the reactants, especially for the catalyst, have been insufficiently defined in many cases, and, frequently, only in a qualitative manner. Unfortunately, it is extremely difficult to determine with any degree of accuracy the small amounts of moisture and/or hydrogen halide which may be associated with the metal halide, despite rigorous methods of purification.

For a given unsaturate and metal halide, there undoubtedly exists a minimum or threshold amount of cocatalyst necessary to initiate reaction. For a condensed system involving a reactive monomer such as isobutylene and a strong metal halide like boron trifluoride, reaction invariably occurs, since removal of cocatalyst below the minimum amount necessary for activation cannot be accomplished. In the gaseous phase, more "completely anhydrous systems" may be realized and thus the reactivity of isobutylene has been materially arrested in the presence of boron trifluoride and absence of added cocatalyst. On the other hand, when employing the same monomer in the condensed phase with a less active catalyst such as titanium tetrachloride, the amount of attendant moisture or hydrogen halide generated in situ is apparently insufficient for activation. Unfortunately, no standards of procedure or purification techniques have been extensively and commonly practiced so that both gaseous and condensed systems may vary considerably with regard to the amount of moisture and/or hydrogen halide that may be present. Nevertheless, it is fairly certain that in the presence of a cocatalyst a tricomponent system is involved, and that the maximum rate will be a function of the concentration of monomer, metal halide, and cocatalyst, and of the initial temperature.

Mechanism of Dehydrohalogenation

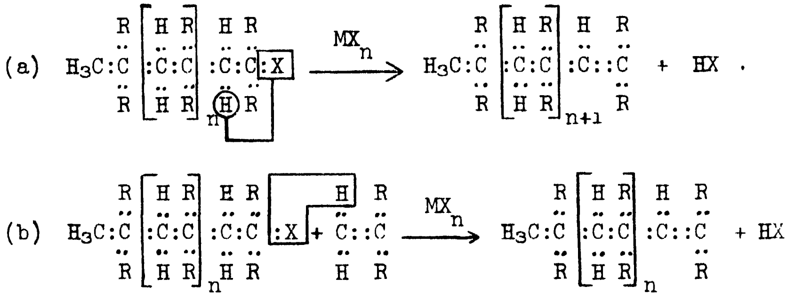
Stanley (46), Nash (47), Ipatieff (48), and Hall (49), have suggested that the initiation of polymer growth among unsaturated hydrocarbons may proceed through the addition of hydrogen halide, the same being catalyzed by electrophilic metal halides. This would be followed by reaction of the alkyl halide thus formed with a molecule of unsaturate, and hydrogen halide would be eliminated. The resulting dimer would further react with another molecule of hydrogen halide to produce a higher alkyl halide. Thus, chain growth would be realized through repeated addition of hydrogen halide followed by intermolecular dehydrohalogenation. The termination step would involve, in all probability, either an intramolecular dehydrohalogenation or an intermolecular dehydrohalogenation similar to one of the alternate steps in the propagation. Terminal unsaturation would result in either case. The following equations illustrate the proposed mechanisms.

Initiation and Propagation.



where HX is hydrogen halide and MX_n the electrophilic metal halide.

Termination.



While the addition of hydrogen halide to unsaturates takes place at temperatures well below zero degrees in the presence of electrophilic metal halides (43), it is highly improbable that catalyzed addition of hydrogen halide followed by intermolecular dehydrohalogenation would result in the degree of polymer growth realized under the reaction conditions employed. In fact, the extremely rapid rate associated with polymer growth at low temperatures in the presence of electrophilic metal halides would militate against accepting a mechanism which involved dehydrohalogenation as one of the principal growth steps.

Higher alkyl halides (i.e., n-butyl chloride), when used as solvents, have been found to arrest markedly the activation of a reactive monomer like alpha-methylstyrene (50). Furthermore, since hydrogen halides have been shown to inhibit markedly the degree of growth and ultimate yields, it is highly improbable that they would constitute the active factor in the initiation and propagation steps associated with the extensive growth realized in low-temperature polymerization.

SUMMARY

Observations, both qualitative and quantitative, on the polymerization of unsaturated hydrocarbons in the presence of electrophilic metal halides indicate a mechanism which involves active participation of a cocatalyst in certain specific cases. Both acids and water have been found to be active cocatalysts, the possibility existing that the latter, in the presence of a metal halide, generates hydrogen halide in situ. In cases involving a cocatalyst, complex formation between metal halide and cocatalyst is pictured as furnishing the proton necessary for activation. Carbonium ion formation is postulated in the initiation step, although it is possible that a dual mechanism (cationic-anionic) may function, the same accounting, perhaps, for the presence of catalyst residues invariably associated with the polymeric product.

In cases in which polymerization is apparently realized in the absence of added cocatalyst (e.g., liquid-phase polymerization of isobutylene with boron trifluoride), it is rather probable that an extremely small amount of water and/or hydrogen halide is present despite rigorous purification, this amount being sufficient to initiate growth. It has been proposed, therefore, that for a given monomer—catalyst combination, there exists a minimum or threshold amount of cocatalyst necessary to initiate growth, and results to date have indicated marked differences in activity among the various combinations of catalyst and cocatalyst examined. The dissociation of the complex to yield the requisite concentration of chain-initiating ions apparently constitutes the critical step.

In the carbonium ion mechanism, the mode of termination for growing chains requires clarification. Neither unimolecular cessation resulting from the ejection of a proton (terminal unsaturation) nor termination by a hydroxyl ion (saturated product) accounts for the catalyst residues invariably associated with polymers prepared in the presence of metal halide catalysts. The dual mechanisms (cationic-anionic) functioning in the presence of a cocatalyst may account for the catalyst residues, since a bimolecular termination involving positive and negative chains would produce a product containing the conjugate base fragment.

It is evident that some form of standardization with respect to methods of purification of reactants appears desirable, since the reactivity and ultimate physical properties may be markedly affected in the presence of water and/or hydrogen halide.

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Synopsis

The mechanism presented constitute proposals made in attempts to portray the role that electrophilic halides play in catalyzing the polymerization of unsaturated hydrocarbons. All of these halides require the presence of a Friedel-Crafts catalyst in the reaction mixture and differ primarily in the interpretation of what constitutes the active factor in the initiation, propagation, and cessation steps. Mechanisms involving a thermal activation and dehydrohalogenation are discussed briefly and rejected as rather improbable. On the other hand, mechanisms involving a cationoid complex intermediate and a carbonium ion are extensively reviewed, especially in light of the recent findings of British investigators regarding the function of the so-called third component or cocatalyst. Attention is called to the rather marked specificity of reactions involving water or other polar cocatalysts, and, in addition, it is pointed out that, although cocatalysts appear to be necessary prerequisities for activation in a number of cases, the phenomenon is not a general one, since systems exist in which proton-supplying cocatalysts have not been proved necessary to initiate growth. To date, no single mechanism seems to satisfy all of the qualitative observations and known data. It is intended that the present discussion summarize available facts in terms of possible mechanisms, and, in addition, evaluate their plausibility in the light of present knowledge.

Résumé

Les mécanismes présentés essaient d'interpréter le rôle, qu'exercent les halogénures électrophiles dans la catalyse de la polymérisation des hydrocarbures non-saturés. Tous ces halogénures nécessitent la présence d'un catalyseur du type Friedel-Crafts dans le mélange réactionnel; l'interprétation concernant le facteur actif dans les étapes d'initiation, de propagation et de rupture sera donc fondamentalement différente. Des mécanismes, comportant une activation thermique et une déshydrogénation, sont brièvement discutés, et réfutés parce que plutôt improbables. D'autre part, la formation de complexe intermédiaire cationoïde et la formation d'un ion carbonium sont tout spécialement envisagées à la lumière des récentes découver-

tes des chercheurs anglais sur le rôle des cocatalyseurs. L'attention est attirée sur la spécificité plutôt marquée des réactions comprenant de l'eau ou d'autres cocatalyseurs polaires; en plus, bien que les cocatalyseurs semblent être conditions nécessaires à l'activation dans beaucoup de cas, ce phénomène n'est pas général, puisqu'il existe des systèmes dans lesquels les cocatalyseurs, donneurs de protons, ne semblent pas nécessaires pour entamer la croissance. Actuellement un mécanisme simple ne peut satisfaire toutes les observations qualitatives, ni les données connues. Cet exposé actuel a pour but de résumer les faits disponibles dans le cadre des mécanismes possibles, et, en outre, d'estimer leur plausibilité à la lumière des connaissances actuelles.

Zusammenfassung

Der vorgeschlagene Reaktionsmechanismus versucht, die Rolle von elektrophilen Haloiden bei der Katalyse der Polymerisation von ungesättigten Kohlenwasserstoffen zu erklären. Alle diese Haloide verlangen die Gegenwart von Friedel-Crafts-Katalysatoren in der Reaktionsmischung und unterscheiden sich hauptsächlich in der Definition des aktiven Faktors für die Anfangs-, Fortführungs-, und Endstufe der Reaktion. Mechanismen, die eine thermische Aktivierung und Dehydrohalogenierung erforden, werden kurz erörtert und als unwahrscheinlich verworfen. Andrerseits werden Mechanismen, die ein kationisches Komplex-Zwischenprodukt und ein Carbonium-ion benutzen, ausführlich besprochen, speziell im Lichte von Untersuchungen von Britischen Forschern, die die Funktion von sogenannten dritten Komponenten oder Co-Katalysatoren erörtern. Es wird auf die ziemlich ausgesprochene Spezifität der Reaktionen, die Wasser oder andere polare Co-Katalysatoren benützen, aufmerksam gemacht, und es wird ferner bemerkt, dass, obwohl Co-Katalysatoren notwendigevoraussetzungen für die Aktivierung in einer Reihe von Fallen zu sein scheinen, diese Beobachtung nicht eine allgemeine ist, da Systeme existieren, in denen Protonen-liefernde Co-Katalystoren sich für das Anlassen von Kettenwachstum als unnötig erwiesen haben. Augenblicklich scheint kein einziger Mechanismus alle qualitativen Beobachtungen und Zahlenwerte zu befriedigen.

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Preparation and Properties of Rubberlike High Polymers.

VI. Polymerization and Dimerization of Isoprene*

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INTRODUCTION

The preparation of polyisoprene has been discussed in Parts I (1) and III (2), while the mechanical properties of polyisoprene have been compared with other polymers in Part IV (3) and those of the copolymers with isoprene in Part V (4) of this series. In the present paper we shall deal with various theoretical aspects of isoprene chemistry. The course of dimerization reactions gives new information on the properties of conjugated double bonds (5). It is necessary to inhibit polymerization completely before proceeding with a quantitative study of dimerization. We have therefore made a survey of a great number of compounds, which influence the course of polymerization reactions. The results that differ somewhat from those found with polyvinyl compounds, will be discussed in the first paragraph. Quite incidentally we found that isoprene itself can act as inhibitor in vinyl polymerization, as will be shown in paragraph IV. After discussing dimerization we shall make some final comments on the properties of polyisoprene, comparing our data with the more extensive work of American authors.

EXPERIMENTAL

Two sources of isoprene were used: (a) a product made from natural rubber (6) and purified via the sulfone; b.p. 34.0–34.3°C.; n_D^{20} = 1.4228; and (b) a trade product purified by distillation; b.p. (760 mm.) 33.8–34.4°C.; n_D^{20} = 1.4217. The reaction of this isoprene with maleic anhydride gave a yield of 100 ± 2% and the content of active oxygen was 4–6 p.p.m. after distillation. Polymerization and dimerization were carried out in sealed test tubes with 5–10 g. samples. The amount of polymer was determined by precipitation in alcohol. The dimer was finally prepared in 50–100 g. batches, analyzed by fractionation, and identified as the silver nitrate complex and as the hydrochloride (see below).

Dimerization and polymerization rates at high temperatures were followed by measuring the contraction in sealed thin tubes of 20-cm. length. As the viscosity of the dimer is not essentially different from that of the monomer, an increase in relative viscosity in these tubes is a relative measure of polymerization.

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Properties of the polymers were compared as discussed in previous papers. Relative plasticity was measured with the steam plastometer. Solubility and swelling in chloroform and benzene were used as a measure of cross linking, while tackiness of the polymer and viscosity of the dilute solution served as a measure of the molecular size. Quality was judged on this basis by a relative scale from 0 to 6: 0 = oily liquid, 1 = viscous plastic, 3 = weakly elastic and soluble, 4 = 3 but partly insoluble, 6 = insoluble, swollen in chlorofrom and elastic.

I. INHIBITORS AND INITIATORS

Our first aim was the evaluation of a strong inhibitor suitable for a quantitative study of dimerization. Results are summarized in Table I. The formation of a rubber in the blank takes place even in a tube filled with purified nitrogen, and is probably due to the presence of traces of peroxides. This type of polymerization comes to a standstill after 3 days. 1% of picric acid (7) inhibits the reaction completely. At higher temperatures, 125°–150°C., picric acid is still very efficient. but a certain amount of resinification takes place in secondary reactions. Trinitrobenzene is nearly as effective while other nitro compounds are inefficient. Metal nitrates, on the other hand, have either as such, or through the formation of nitrites, a considerable initiator activity.

Hydroquinone and pyrogallol (in group B of Table I) are slightly less effective than picric acid. Other quinones do not reduce the yield in comparison with the blank but lower the quality, a result indicating chain transfer activity. This effect is still more pronounced with iodine compounds (group C of Table I), which yield oils rather than rubbers.

Sulfur compounds (group D of Table I), well known as chain transfer agents, form the borderline between inhibitors and initiators. Sulfur itself has a distinct accelerating action on isoprene.

Our earlier experience (Part I) is confirmed by the results summarized in Table II. Acids as well as a well-known antioxidant (No. 18) act as weak initiators. Peroxides are moderately effective and yield soft and sticky products. Another source of radicals (No. 24 in Table II) is also less active with isoprene than with vinyl compounds.

The azo compounds (group C of Table II) are likewise of little value and the only remaining group is the azoamino compounds, which combine the ability to initiate polymerization with the tendency to form cross links. Diazoaminobenzene is more effective than any of the others in this group. The formation of phenyl radicals is probably an essential step in the initiation.

The well-known correlation between reaction rate and square root of initiator concentration has been found to hold also for pure isoprene (see Table III). The high yield after a relatively short time is reached only at the expense of quality, (see Fig. 1). Both results are in good agreement with present theories of polymerization.

We have studied the activity of some of the initiators and inhibitors at 150°C. with the aim of elucidating the simultaneous occurrence of dimers and polymers at this temperature.

The formation of a very soft polymer induced by 0.1% diazoaminobenzene at 150°C. is complete after 2-3 hours. Benzoyl per-

oxide, on the other hand, is so ineffective that dimerization becomes preponderant. In the presence of 1% of the iodine compounds Nos. 11, 12, 13, or the sulfur compounds, Nos. 14 and 16 of Table I, only 20% polymer is formed; the rest consists of liquid dimers. These reagents, however, interact with the dimers as can be concluded from the presence of sulfur and iodine compounds in the liquid fraction. The only useful inhibitors proved to be picric acid and pyrogallol. The influence of concentration is very pronounced; 0.1% inhibitor at 150°C.

TABLE I. Inhibitor and initiator activity of nitro compounds, phenols, iodine, and sulfur compounds, at 100 °C., with pure isoprene

No.	Compound	Polymer				Type of activity
		Reaction time				
		3 days		11 days		
		Yield	Quality	Yield	Quality	
1	Blank	20	2	21	3	-
	A. Nitro Compounds					
2	Picric acid	0.0	-	0.3	0	Strong inhibitor
3	Trinitrobenzene	3	1	5	1	" "
4	Nitronitrosobenzene	12	1	19	1	Chain transfer
5	Lithium nitrate	33	2	48	4	Initiator
6	Silver nitrate	37	2	66	4	"
	B. Polyphenols					
7	Hydroquinone	0.0	-	3	0	Strong inhibitor
8	Di-tert-amylhydroquinone	11	1	15	1	Chain transfer
9	Pyrogallol	2	0	5	0	Strong inhibitor
10	Chloranil	17	1	25	1	Chain transfer
	C. Iodine Compounds					
11	Iodine	8	0	14	0	Chain transfer
12	Iodoform	17	0	16	0	" "
13	Iodoacetic acid			>16	0	" "
	D. Sulfur Compounds					
14	Thioacetic acid	14	2	20	2	Chain transfer
15	Thiourea	14	3	26	3	Weak initiator
16	Thiophenol	15	2	34	2	" "
17	Sulfur	29	2	47	2	" "

becomes ineffective and can even act as a weak initiator of polymerization. With copper oleate such changes from an effective initiator even at a concentration of 1% to a strong inhibitor at 5% concentration are similar to the effect of concentration in the "antioxygene" studies of Dufraise and his school.

TABLE II. Weak and Strong Initiators for Isoprene at 100°C.

No.	Compound	Polymer				Type of activity
		Reaction time				
		3 days		11 days		
		Yield	Quality	Yield	Quality	
1	Blank	20	2	21	3	-
	A. Acids and Bases					
18	Phenyl β-naphthylamine	11	2	30	2	Weak initiator
19	Acetic acid	24	3	49	4	Initiator
20	Acetoacetic ester	29	2	50	3	"
	B. Peroxides and Related Compounds					
21	Benzoyl peroxide	42	2	60	2	Initiator
22	Ascaridole	36	2	62	4	"
23	Tetralin peroxide	49	2	75	2	Strong initiator
24	Tetraphenylsuccinic acid dinitrile	36	2	36	2	Weak initiator
	C. Azo Compounds					
25	Hydrazobenzene	5	1	7	1	Inhibitor
26	Azobenzene	16	2	30	2	Weak initiator
27	2-Methylbenzimidazole	11	1	20	1	Chain transfer
	D. Azoamino Compounds					
28	Diazoaminobenzene	69	4	75	6	Strong initiator
29	Na salt of No. 28	44	3	74	6	" "
30	N-benzyl derivative of No. 28	56	3	75	6	" "
31	p-Diazotolueneaniline	49	3	73	6	Strong initiator
32	p-Diazotoluene-p-toluidine	46	3	69	6	" "
33	Bis-(benzene diazo)methylamine	61	3	68	5	" "

The difference in the kinetics of high-temperature diene and vinyl polymerization should be emphasized. At 150°C. isoprene dimerizes with a half-time of about 4 hours. This reaction is purely thermal and not influenced by the presence of an inhibitor. Polymerization can occur only if it is very fast. The molecular size of the polymer will be influenced by the inhibitor properties of the dimer (8). The thermal polymerization of styrene, on the other hand, can be delayed, for example, by the presence of 1% pyrogallol for about one hour. No reaction occurs during this time until the inhibitor has been used. However, a mixture of low viscosity, consisting of solid and liquid polymers, can be produced from styrene by heating it in the presence of 1 g. iodine or iodoform at 200°C. A polymerization-depolymerization equilibrium seems to be established under the catalytic influence of iodine at 200°C., completely comparable to the action of oxygen at lower temperature (9).

TABLE III. Correlation between Yield and Initiator Concentration for Isoprene at 100° C. Using n Per cent Diazoaminobenzene (Half-Time for Polymerization in Hours)

n, per cent D.A.B.	0.1	0.5	1.0	2.0
Hours	192.	79.	55.	36.
Relative rate	0.31	0.8	1.1	1.6
$\sqrt{n}$	0.32	0.7	1.0	1.4

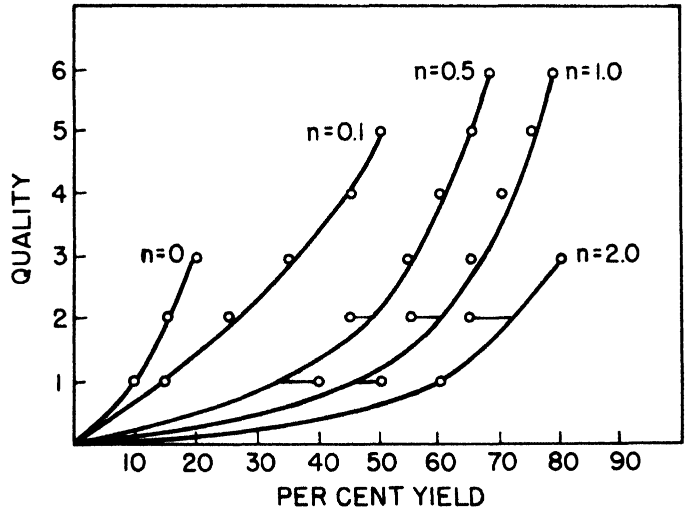


Fig. 1. Influence of initiator concentration (n% diazoaminobenzene) on relative quality of polyisoprene.

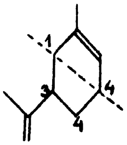
II. THE DIMERIZATION OF ISOPRENE

We have tried to separate dimerization and polymerization by the action of picric acid. On heating isoprene at 130°C., 90 conversion is reached after 160 hours. The polymers can be separated into 80% dimers and 13% of a rubber (relative quality 3). About 7% higher boiling material and benzene-soluble resins are formed in side reactions. This result is in good agreement with the experience of previous authors (10). As expected it is possible to inhibit polymer formation completely by the addition of 1% picric acid. Results are summarized in Table IV. No trimers or higher boiling materials are formed at the time of 50% dimerization, but resinification sets in on further heating between 100 and 150°C. The data of Table IV suggest a reaction higher than second order and a large energy of activation.

TABLE IV. Dimerization of Isoprene Stabilized with 1% Picric Acid

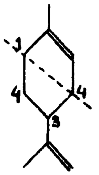
Temperature, °C.	Time, hours	Percent dimers	Percent polymers
100	24	11	0
	72	24	0
	168	43	0.2
	408	70	17
	1632	79	21
125	24	42	0.2
	48	59	0.4
	96	70	4.4
	160	84	6
150	0.34	49	0.2
	24	70	5
	48	74	11
200	24	60	32

It has been known for a considerable time that the 4 possible carbon skeletons of the dimer are formed in different yields. The position of the double bonds in the 4 isomers is uncertain, due to a possible allylic rearrangement. Lebedew (10a) separated the higher boiling mixture, (I) + (II), from a lower boiling compound to which he assigned structure (III), but which could also be a mixture of (III) and (IV).



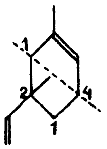
(I)

Diprene



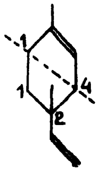
(II)

Dipentene



(III)

Lebedew



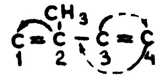
(IV)

Wagner-Jauregg (10b) proved the preponderance of the diprene (I) in the higher boiling fractions. We can confirm these results and add the following methods for a quantitative separation.

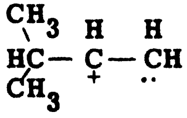
a. (I) can be separated from (II) by the action of aqueous silver nitrate. (I) dissolves in this reagent and forms a high-melting complex compound, while (II) neither dissolves nor crystallizes with silver nitrate.
b. The solid (trans) dihydrochloride from (II) has a similar melting point to that of the solid dihydrochloride from (I), but on mixing the hydrochlorides a considerable depression is observed. In addition to the solid, an isomeric liquid dihydrochloride from (I) (probably the cis isomer) is formed.
c. (III) and (or ?) (IV) are soluble in aqueous silver nitrate but do not crystallize. The reaction with hydrochloric acid yields only a monochloride. The double bond in this monochloride does not add on HCl even at 100°C. under pressure; this result is in good agreement with structures (III) and (IV).

A detailed discussion of these results will be given elsewhere but the following preliminary estimate of yields already permits some new conclusions. Yields: (I) $\overset{=}{<}$ 80%; (II) $\overset{=}{<}$ 5%; (III) and (or) (IV) $\overset{=}{<}$ 10%.

The electronic formulation of isoprene (11) allows for the ex-



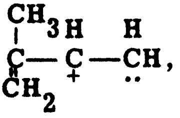
planation of the donor properties of the 1-carbon atom and the acceptor properties of the 3,4 double bond (12). As has already been discussed in another paper (13) the reactivity of the 3,4 double bond at 150°C. corresponds to that of the double bond in maleic anhydride at 20°C. The difference in yields indicates that the 3,4 double bond is about 10 times more reactive as an acceptor than the 1,2 double bond. While this result is in good agreement with the electronic concept, we find a rather surprisingly large difference in the yields for (I) and (II). The formation of dipentene occurs less readily than the formation of Lebedew's hydrocarbon. In other words the pair of electrons from C-1 add on almost exclusively to C-3 and only very rarely to C-4, thus leading to diprene as the main reaction product. Comparing the structures (V) and (VI):



$$\underset{CH_3}{\overset{CH_3}{HC}}-\underset{+}{\overset{H}{C}}-\underset{\cdot\cdot}{\overset{H}{CH}}$$

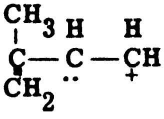
V

and



$$\underset{CH_2}{\overset{CH_3}{C}}-\underset{+}{\overset{H}{C}}-\underset{\cdot\cdot}{\overset{H}{CH}},$$

VI



$$\underset{CH_2}{\overset{CH_3}{C}}-\underset{\cdot\cdot}{\overset{H}{C}}-\underset{+}{\overset{H}{CH}}$$

VII

we can draw the following conclusions.

1. The overall availability of π-electrons in (VI) is much smaller than in (V), this effect being due to resonance.
2. The distribution of charge, making the C-3 atom positive, is the same in both olefins. The direction of addition to the 3,4 - double bond in isoprene corresponds, therefore, mainly to the addition rules for polar reactions, involving mono-olefins. The reverse structure (VII) reacts only to a very small but measurable extent isoprene addition and, as far

as we know, not at all in other polar reactions such as HCl addition.

III. POLYISOPRENE

We have shown in Parts IV and V of this series that a close correlation exists between brittle point, elastic recovery, and rebound elasticity of polydienes and their copolymers. Two structural factors are of significant influence: (a) methyl groups in the diene, and (b) 1,2 addition or vinyl copolymerization leads to a decrease of molecular flexibility and therefore to an increase in brittleness. The importance of the influence of other structural factors on mechanical propties can be deduced from a study of tensile strength. This becomes evident from a recent survey by d'Ianni (14). Isoprene, polymerized with a special metal catalyst, has a similar content of vinyl side groups (form 1,2 addition) to that of emulsion polyisoprene and a similar brittle point, but a much higher tensile strength. We can confirm these results as far as the properties of emulsion polymers are concerned and can add that the properties of bulk polymers are quite similar. Polyisoprene made with 0.1-0.5% diazoaminobenzene had promising mechanical properties as a raw rubber (see Fig. 1), but the average tensile strength of a carbon black mixture did not exceed 75 kg./cm.^{2} at 450% elongation at break. In fact we were unable to produce a fair rubber from polyisoprene. This confirms the opinion (14) that polymolecularity as well as unknown details of the chain structure in polyisoprene is essential for a high tensile value.

The addition of hydrochloric acid to the polymer has been used (14) as a measure of the total 1,4 and 3,4 polymerization. We can confirm the usefulness of this method and also that the number of 1,4 + 3,4 polymer units was found to be independent of experimental conditions in bulk and emulsion polymerization.

IV. THE INHIBITOR ACTION OF ISOPRENE

It is a well-known phenomenon that a vinyl compound acts as a retarder in the polymerization of a second vinyl compound. This effect is probably due to the intermediate formation of a resonance-stabilized radical, and cannot therefore be explained in general terms. The copolymerization of 1,1-dichloroethylene with dienes and other vinyl compounds has been frequently studied in the course of applied as well as fundamental research. From the available data the impression is gained that this process does not differ essentially from other diene-vinyl-copolymer systems. This probably true for the propagation step in systems with the diene as the main phase. We have found quite incidentally that the situation changes abruptly when a small quantity of isoprene is added to dichloroethylene. Figure 2 gives a survey of yields at constant reaction time, and Figure 3 illustrates the inhibitor activity of isoprene during very long reaction times. Even at high isoprene concentrations the propagation chain is essentially carried by the added isoprene. This follows from the composition of the polymers. They show a large deficiency of dichloroethylene units (see Fig. 4).

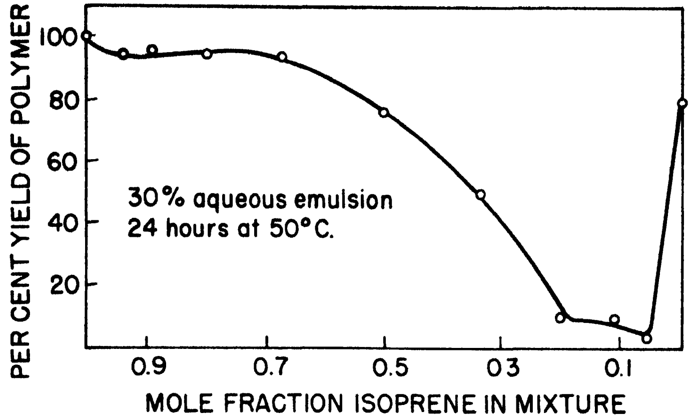
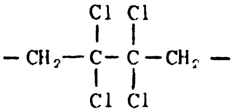


Fig. 2. Inhibitor action of isoprene on polymerization of pure 1,1-dichloroethylene. 1% H_2O_2 with fixanol as emulsifier.

Kinetic analysis (unpublished results, see 15) of the products, makes it probable that units of the type:



$$-CH_2-\overset{Cl}{\underset{Cl}{C}}-\overset{Cl}{\underset{Cl}{C}}-CH_2-$$

are inserted between the isoprene chains and not only the head-tail structures present in vinylidene chloride polymers. Analogous experments in bulk polymerization lead to identical conclusions.

Using 1% diazoaminobenzene or 1% benzoyl peroxide it is possible to polymerize dichloroethylene at 100°C. in a few hours. Addition of 0.5 mole per cent isoprene is sufficient to inhibit polymer-

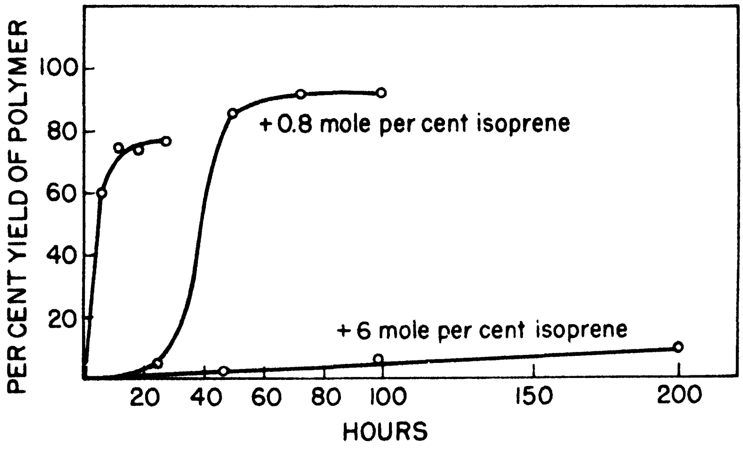


Fig. 3. Influence of isoprene concentration on inhibitor action in the polymerization of pure 1,1-dichloroethylene (left-hand curve). Emulsion as in Figure 2. Time variable.

ization. A few per cent of polymers are formed in the beginning, but the reaction thereafter comes to a complete standstill. One can follow this phenomenon conveniently by measuring the contraction and viscosity of the liquid - monomer mixtures.

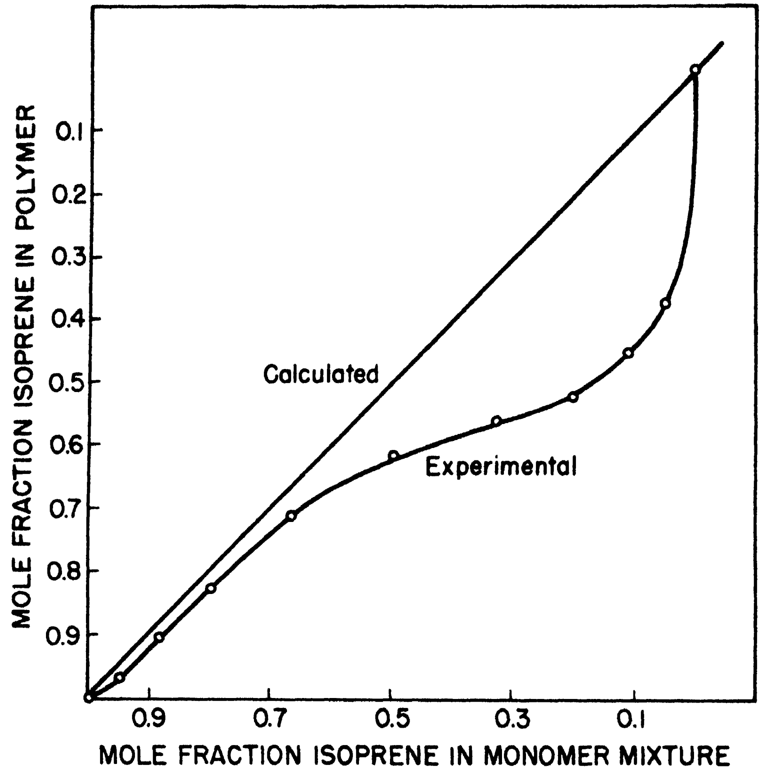
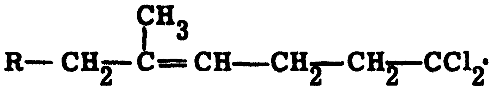


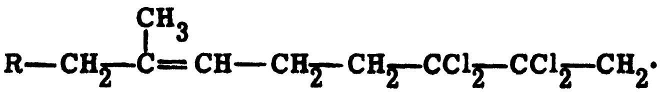
Fig. 4. Chlorine deficiency in copolymers from isoprene and 1,1-dichloroethylene. Emulsion as in Figure 2. 24 hours at 50°C.

The present knowledge of radical reactivity is, in our view, not sufficiently developed to predict these curious results. A tentative explanation ad hoc is the following. The radicals (VIII and (IX):

(VIII)


$$R-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_2-CCl_2\cdot$$

and

(IX)


$$R-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_2-CCl_2-CCl_2-CH_2\cdot$$

are so much stabilized that chain termination supercedes chain propagation. Taking the selective action of $\cdot CCl_3$ and similar radicals into account, this explanation seems also feasible in terms of electronic structure.

Another cause of inhibition will be an occasional transfer of a hydrogen atom from isoprene to the growing radical chain. The resulting new allyl-type radical from isoprene is too stable (16) to carry on the reaction chain.

Acknowledgment

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Synopsis

The inhibitor and initiator action of 33 compounds on the bulk polymerization of pure isoprene has been studied. Picric acid was found to be the most powerful inhibitor at 100°C. The conclusion reached in Part I, that the initiator activity of diazoaminobenzene is superior to all other compounds has been found to be valid also between 100-150°C. The heat polymerization of isoprene between 100-150°C. in the presence of picric acid leads only to the formation of dimers. Three of the four possible isomers have been separated. The solid complex compound of diprene (I) with silver nitrate has been used to separate it from dipentene (II) and the hydrocarbon of Lebedew (III, IV) has been identified as a monochloride. The relative yields (I):(II):(III+IV) = 16:1:2 are in agreement with the relative availability and localization of π-electrons in isoprene. Observations on the properties of polyisoprene are in agreement with the more extensive work by d'Ianni. Some remarks on polymers from bulk polymerization are added. Isoprene acts as a powerful inhibitor on the polymerization of vinylidene chloride. This effect is independent of the method of polymerization.

Résumé

L'effet inhibiteur et intiateur de 33 composés sur la polymérisation en bloc de l'isoprène a été étudié. L'acide picrique est l'inhibiteur le plus énergique à 100°C. La conclusion, obtenue dans le travail précédent, qui supposait l'activité initiatrice du diazoaminobenzène comme la plus élevée, est également valide ici entre les températures de 100-150°. La polymérisation thermique de l'isoprène entre 100°-150° en présence d'acide picrique comme inhibiteur fournit seulement des dimères. Trois des quatre isomères possibles ont été isolés. Le complexe solide du diprène (I) avec le nitrate d'argent a été utilisé comme moyen de séparation du dipentène (II); l'hydrocarbure de Lebedew (III et IV) a été identifié sous forme de monochlorure. Les rendements relatifs de (I):(II):(III+IV) = 16:1:2 sont en accord avec la disponibilité et la localisation des électrons-π dans l'isoprène. Les propriétés du polyisoprène sont en accord avec les observations plus étendues d'Ianni. Certaines remarques concernant les polymères, provenant de polymérisations en bloc, sont ajoutées. L'isoprène agit comme inhibiteur énergique sur la polymérisation du chlorure de vinylidène. Cet effet est indépendant de la méthode de polymérisation.

Zusammenfassung

Die Wirkung von 33 Verbindungen als Inhibitor oder Beschleuniger auf die Blockpolymerisation von reinem Isopren wurde untersucht. Pikrinsäure erwies sich als der kräftigste Inhibitor bei 100°C. Diazoaminobenzol ist zwischen 100-150°C. der kraftigate Inhibitor (siehe auch Teil I). Die Wärmepolymerisation des Isoprens zwischen 100-150°C. in Gegenwart von Pikrinsäure führt ausschliesslich zur Bildung der Dimeren. 3 von den 4 möglichen Isomeren wurden getrennt. Die feste Komplexverbindung von Dipren (I) mit Silbernitrat wurde zur Abtrennung von Dipenten (II) benutzt. Der Kohlenwasserstoff von Lebedew (III, IV) wurde als Monochlorid identifiziert. Die relativen Ausbeuten I:II:(III+IV) = 16:1:2 sind in Übereinstimmung mit der relativen Zugänglichkeit und Lokalisierung der π-Elektronen in Isopren. Beobachtungen über die Eigenschaften von Polyisopren stimmen überein mit den ausführlichen Untersuchungen von d'Ianni. Einige Bemerkungen über Block-polymere werden zugefügt. Isopren wirkt als ein kräftiger Inhibitor auf die Polymerisation des Vinyliden chlorids. Dieser Effekt ist unabhängig von der gewählten Polymerisationsmethode.

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LETTER TO THE EDITORS

COPOLYMERIZATION OF SOME FURTHER MONOMER PAIRS

Continuing the studies of copolymerization previously reported (1-5), we have investigated the copolymerization behavior of the following monomer pairs: (a) styrene/vinyl carbazole, (b) methyl methacrylate/vinyl carbazole, (c) styrene/1,2-dichloro-2-propene, (d) methyl methacrylate/1,2–dichloro–2–propene. The reactivity ratios obtained for these systems are reported in Table I.

TABLE I. Reactivity Ratios*

System No.	M_1	M_2	r_1	r_2
I	Styrene	Vinyl carbazole	5.5	0.012
II	Methyl methacrylate	Vinyl carbazole	2.0	0.20
III	Styrene	1,2-Dichloro-2-propene	5.0	0.06
IV	Methyl methacrylate	1,2-Dichloro-2-propene	5.5	0.17

*Estimated probable errors in r_1 and r_2 values: ±15% of reported values.

Experimental

Styrene was purified by several washings with dilute sodium hydroxide, followed by several washings with distilled water. It was later dried over calcium chloride and distilled under vacuum. Methyl methacrylate and 1,2-dichloro-2-propene (supplied by Halogen Chemicals) were purified by simple vacuum distillation. Vinyl carbazole was purified by crystallization from petroleum ether.

Pairs of monomer mixtures were prepared over the entire range of composition, sealed in glass tubes and placed in a constant-temperature water bath maintained at 70°C. All mixtures contained 0.1% by weight of benzoyl peroxide as the catalyst. Polymerization was allowed to proceed until a conversion of about 5% had taken place.

The copolymers were purified by precipitating in methanol and redissolving in methyl ethyl ketone, and reprecipitating several times, followed by "benzene freezing" (6) and vacuum drying at 45°C. The copolymers containing 1,2-dichloro-2-propene were analyzed for chlorine whereas those containing vinyl carbazole were analyzed for nitrogen by the micro-Dumas method.

The following tables, Systems I through IV, indicate the composition of the initial monomer mixture, the chlorine or nitrogen analysis and the molar composition of the copolymer.

System I. Styrene (M_1) - Vinyl Carbazole (M_2)

M_2*	Per cent nitrogen in polymer	m_2**
0.0445	0.16	0.012
0.1160	0.28	0.021
0.3226	0.87	0.068
0.8256	2.70	0.242
0.9280	4.20	0.426
1.0000	7.15	0.975

System II. Methyl Methacrylate (M_1) - Vinyl Carbazole (M_2)

M_2*	Per cent nitrogen in polymer	m_2**
0.1150	0.94	0.072
0.3230	2.40	0.204
0.5056	2.98	0.266
0.8950	5.63	0.643
0.9210	6.00	0.713

System III. Styrene (M_1) - 1,2-dichloro-2-propene (M_2)

M_2*	Per cent chlorine in polymer	m_2**
0.0752	1.47	0.022
0.1940	3.34	0.049
0.5850	16.17	0.241
0.7961	25.20	0.379
0.9131	35.00	0.532
0.9350	37.60	0.573

System IV. Methyl Methacrylate (M_1) - 1,2-Dichloro-2-propene (M_2)

M_2*	Per cent chlorine in polymer	m_2**
0.0730	0.99	0.014
0.1841	2.39	0.034
0.3740	6.81	0.097
0.7821	27.28	0.402
0.9140	41.40	0.624

*Mole fraction (M_2) in monomer mixture.
**Mole fraction (m_2) in copolymer.

Discussion of Results

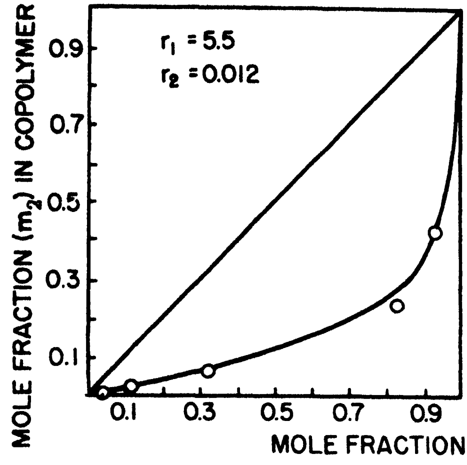

Fig. 1. Copolymer composition curve for the system styrene (M_1)-vinyl carbazole (M_2).

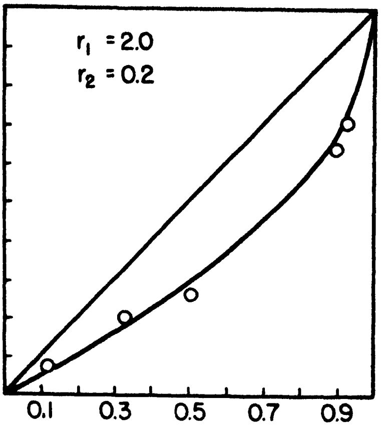

Fig. 2. Copolymer composition curve for the system methyl methacrylate (M_1)-vinyl carbazole (M_2).

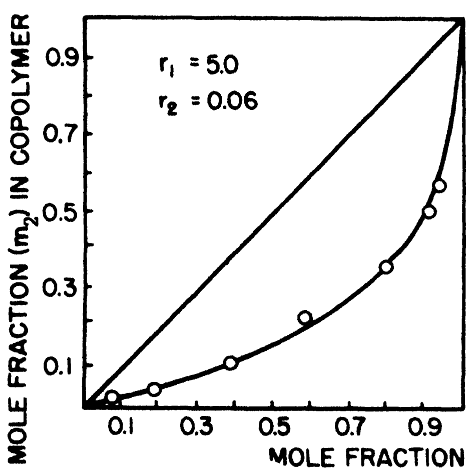

Fig. 3. Copolymer composition curve for the system styrene (M_1)-1,2-dichloro-2-propene (M_2).

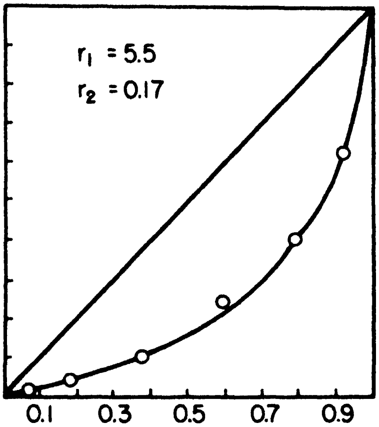

Fig. 4. Copolymer composition curve for the system methyl methacrylate (M_1)-1,2-dichloro-2-propene (M_2).

The experimental results of the above four systems are in Figures 1-4, respectively. From these studies we can make the following observations.

(a) Styrene monomer adds both to its own radical and to a vinyl carbazole radical (or 1,2-dichloro-2-propene radical) at a considerably faster rate than does vinyl carbazole monomer (or 1,2-dichloro-2-propene monomer). Vinyl carbazole and 1,2-dichloro-2-propene monomers have approximately equal tendencies to add to a styrene radical.

(b) Methyl methacrylate, in its copolymerization with vinyl carbazole or 1,2-dichloro-2-propene, follows the general pattern of styrene. However, vinyl carbazole monomer adds to a methyl methacrylate radical nearly two and a half times as fast as does a 1,2-dichloro-2-propene monomer.

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LETTER TO THE EDITORS

KINETICS OF CONDENSATION POLYMERIZATION

Attention is called to three theoretical relations that appear to be in convenient form for the characterization of bimolecular condensation polymerizations by purely physical methods that do not require isolation of the polymer. Generalizations of this kind were recently suggested by Oster (1).

The theory of both statistics and kinetics of the condensation of functional groups on similar molecules has been derived by Stockmayer (2) for the simplest case, that in which (a) the activity of the functional group is not affected by the size of the molecule to which it is attached, (b) functional groups on the same molecule do not react with each other, and (c) the weight loss in condensation is negligible. The statistics yield a relation between extent of condensation and the distribution of molecular sizes of the resultant polymer, while the kinetics yield a relation between the extent of condensation and time elapsed. Combination of the two results gives the following equations (3).

$$\bar{M}_w = M_0 \left[\frac{1 + 2fC_0Kt}{1 + (2f - f^2)C_0Kt} \right] \tag{1}$$

and:

$$\bar{M}_n = M_0 \left[\frac{2 + 2fC_0Kt}{2 + (2f - f^2)C_0Kt} \right] \tag{2}$$

in which C_0 is the initial concentration of monomer of molecular weight M_0 with f functional groups condensing bimolecularly with rate constant K, and $\bar{M}_w$ and $\bar{M}_n$ are the weight-average and number-average molecular weights at time t. Equations 1 and 2 are, due to restrictions on their precursors, valid only up to gelation, which occurs only when $f > 2$. Since at gelation time (t_{gel}), $M_w = \infty$, the denominator of equation 1 must then be equal to zero, whence:

$$t_{gel} = - \frac{1}{C_0K\,(2f - f^2)} \tag{3}$$

A plot of equation 1, with f as parameter and with constant values of M_0, K, and C_0, shows the expected relationships between M_w and t; when $f = 1$, $\bar{M}_w$ becomes asymptotic to $2M_0$ as $t \rightarrow \infty$; when $f = 2$, $\bar{M}_w$ vs. t is a straight line so that $\bar{M}_w \rightarrow \infty$ as $t \rightarrow \infty$; and for $f = 3, 4$, etc., curves of $\bar{M}_w$ vs. t of successively increasing slope are obtained. Gelation occurs at finite values of time, which decrease with increasing values of f. Similarly shaped curves are obtained for

$\bar{M}_n$ from equation 2, but $\bar{M}_n \to \infty$ only when f = 2. Decreasing finite values of $\bar{M}_n$ at gelation are obtained as the values of the parameter f increase from > 2.

It appears from these equations that, with a knowledge of the initial concentration of monomer and the relation of elapsed time to $\bar{M}_w$ (from light-scattering methods) or $\bar{M}_n$ (from vapor pressure methods), the values of K and f could be determined uniquely. One procedure for this would involve calculation of a curve to fit a plot of the experimental data, $\bar{M}_w$ or $\bar{M}_n$ vs. t. Inspection of the shape of the experimental curve would show whether f is 1, 2 or >2. In the latter case, a guess for the value of f would be made, and a value of K satisfying a point on the high molecular weight end of the curve would be calculated. From this pair of values for f and K, an $\bar{M}_w$ or $\bar{M}_n$ would be calculated for a t near the midpoint. If this calculated $\bar{M}_w$ or $\bar{M}_n$ was low or high, appropriate re-estimates of K and f could be made and tried until the calculated curve fitted the experimental one.

If nonintegral values of f should provide the best fit, it is probable that either unequal functional group activity or cyclization or both are present. This point could be checked experimentally (when f >2) without knowledge of K or f by a plot of t_{gel} vs. $1/C_0$ for a series of increasing values of C_0. A straight line would indicate absence of these factors. In any event the nonintegral value of f and its corresponding K would serve as useful characteristics of the reaction in question.

The assistance of Professor W. H. Stockmayer in clarifying certain points discussed in this letter is gratefully acknowledged.

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3. Equations 15 and 16 of reference (2) above were combined with the expression for α on p. 55 of same reference, setting Nk equal to C_0K. In the event of reverse reaction (hydrolysis), a modified expression for α would be used, which could be determined experimentally.

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LETTER TO THE EDITORS

HEAT OF COPOLYMERIZATION

The heat evolved by a polymerization reaction may be regarded essentially as (- Δ H) of the propagation step. In the case of a copolymerization involving monomers M_1 and M_2 there are four distinct propagation steps, each exhibiting its own characteristic heat of reaction.

$$\text{(a)} \quad -M_1^{*} + M_1 \longrightarrow -M_1 - M_1^{*} \qquad \Delta H = \Delta H_{11}$$

$$\text{(b)} \quad -M_1^{*} + M_2 \longrightarrow -M_1 - M_2^{*} \qquad \Delta H_{12}$$

$$\text{(c)} \quad -M_2^{*} + M_1 \longrightarrow -M_2 - M_1^{*} \qquad \Delta H_{21}$$

$$\text{(d)} \quad -M_2^{*} + M_2 \longrightarrow -M_2 - M_2^{*} \qquad \Delta H_{22}$$

ΔH_{11} and ΔH_{22} are the molar heats of polymerization of monomers M_1 and M_2 respectively, and can be measured calorimetrically. The quantities ΔH_{12} and ΔH_{21} cannot be independently determined from the heat evolved in a copolymerization. It is clear that reactions 2 and 3 occur with equal frequency during the reaction, and hence only the sum ($\Delta H_{12} + \Delta H_{21}$) is a calorimetrically measurable quantity.

The enthalpy change in the formation of a sequence of n monomer units of type M_1 is:

$$\Delta H_{21} + (n - 1) \Delta H_{11}$$

At low conversion the number of such sequences is given by:†

$$P_{11}^{n-1} \times P_{12}^{2} \times [\text{total } M_1]$$

where the bracketed quantity refers to the total number of moles of M_1 in the copolymer. The total heat effect associated with all the polymerized M_1 molecules is therefore:

$$\sum_{n=1}^{\infty} [\Delta H_{21} + (n - 1) \Delta H_{11}] (P_{11}^{n-1} P_{12}^{2}) \times [\text{total } M_1]$$

---

†P_{12} is the probability that, during the copolymerization process, a growing free radical chain of the type $-M_1^{*}$ will react with a monomer molecule of type M_2, and similarly for the other P terms. A complete discussion of these propagation probabilities may be found in T. Alfrey, Trans. N. Y. Acad. Sci., 10, 298-303 (1948). An earlier paper discusses the same subject but employs a different type of symbolism (T. Alfrey and G. Goldfinger, J. Chem. Phys., 12, 322 (1944)).

Similarly for the M_2 molecules:

$$\sum_{n=1}^{\infty} [\Delta H_{12} + (n - 1)\Delta H_{22}] \quad (P_{22}^{n-1} \quad P_{21}^{2}) \times [\text{total } M_2]$$

Performing the indicated summations, adding, and dividing by the total number of monomer groups in the copolymer, we get an expression for the molar heat of copolymerization:

$$\Delta H_c = m_1 \quad [P_{12}\Delta H_{21} + P_{11}\Delta H_{11}] + m_2 \; [P_{21}\Delta H_{12} + P_{22}\Delta H_{22}] \qquad (1)$$

where m_1 and m_2 are the mole fractions of the two monomers in the copolymer. Since m_1P_{12} is equal to m_2P_{21}, equation 1 can be written:

$$\Delta H_c = m_2P_{21}(\Delta H_{21} + \Delta H_{12} - \Delta H_{11} - \Delta H_{22}) + m_1\Delta H_{11} + m_2\Delta H_{22} \qquad (2)$$

For the sake of illustration, let us consider the case $\Delta H_{11} = \Delta H_{22} = \Delta H_o$. Let:

$$\frac{\Delta H_{21} + \Delta H_{12}}{2\Delta H_o}$$

be represented by R, so that (2) takes the form:

$$\frac{\Delta H_c}{\Delta H_o} = 2m_2P_{21}(R - 1) + 1 \qquad (3)$$

The quantity of m_2P_{21} can be shown to be of the form:

$$m_2P_{21} = \frac{1 - [1 - 4m_2(1 - m_2)\;(1 - r_1r_2)]^{1/2}}{2(1 - r_1r_2)}$$

so that we have finally:

$$\frac{\Delta H_c}{\Delta H_o} = \frac{1 - [1 - 4m_2(1 - m_2)\;(1 - r_1r_2)]^{1/2}}{1 - r_1r_2}\;(R - 1) + 1 \qquad (4)$$

There are several interesting consequences of equation 4. First, $\Delta H_c/\Delta H_o$ is a function only of (r_1r_2) rather than of the individual values of r_1 and r_2. This is a reasonable result, since (r_1r_2) has been shown to be an index of the alternation tendency in copolymerization. Second, we find by differentiation that when $\Delta H_c/\Delta H_o$ is plotted against copolymer composition for a given R and for various values of (r_1r_2) all the curves in the family have the same initial slope, viz. 2 (R − 1). Finally, since m_2 and $(1 - m_2)$ may be interchanged without changing the value of $\Delta H_c/\Delta H_o$ the curves must all be symmetrical about the central ordinate $m_2 = 0.5$.

The curves in Figure 1 illustrate the various points mentioned above. In all copolymer pairs studied $(r_1r_2) < 1$. In principle R could be either greater or less than unity. However, there is reason to expect R values greater than unity to be the more likely if any appreciable variation from unity occurs.

This analysis applies only for low conversion copolymerization, before appreciable drift in monomer ratio has occurred. Alternately, it gives the instantaneous differential heat of copolymerization at any stage of reaction. The total heat of reaction up to a final conversion could be obtained by an integration procedure.

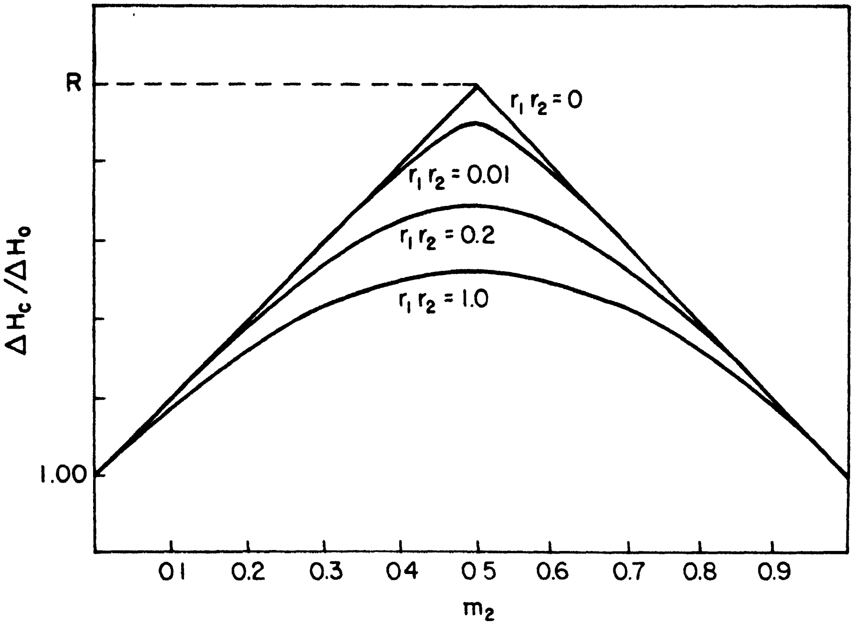

Fig. 1. Heat of copolymerization as a function of composition.

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POLYMER NEWS

A colloquium on macromolecules will be held at Amsterdam on September 2, 3, and 5, 1949. The colloquium will precede the September 6-20 Conference de l'Union Internationale de Chimie and will be under the auspices of the Section Macromolecules of the Union.

A limited number of papers will be read by invited speakers. The main topic is Polymerization Kinetics. The subject of Macromolecules in Solution will also be discussed. Preprints of the lectures will be distributed in advance.

The colloquium was initiated at the suggestion of Professor H. Mark, Brooklyn, New York. The members of the organizing committee are: Prof. Dr. H. R. Kruyt, President; Prof. Dr. J. J. Hermans; Dr. R. Houwink; Dr. C. Koningsberger, Treasurer; Dr. L. J. Oosterhoff; Prof. Dr. J. Th. G. Overbeek; Dr. A. J. Staverman.

Correspondence to the committee should be addressed to P. O. Box 71, Leiden, Netherlands.

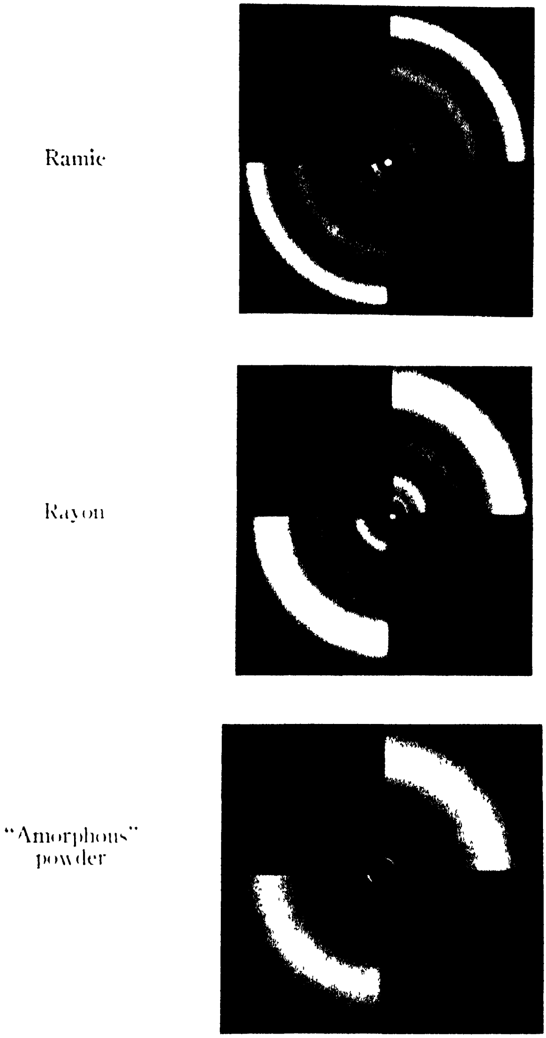
The Conference fee is hfl. 7.50 (approximately $2.85), payable in advance at Incasso Bank, Leiden, to the account of Dr. C. Koningsberger. I. C. M. scientists intending to participate are asked to write to the secretariat. Application blanks with full details about preprints, hotel accommodations, excursions, etc. will be forwarded on request.

* * * * * *

The Institute of Polymer Research and the Division of Applied Physics of the Polytechnic Institute of Brooklyn announce the Sixth Annual Series of Summer Laboratory Courses. The courses offered in the 1949 series are:

June 6-17. Industrial Applications of X-Ray Diffraction
June 27-July 2. Advanced X-Ray Diffraction
June 27-July 1. Molecular Weight Determination of Polymers
July 25-29. Polymerization Techniques

Inquiries should be addressed to Professor I. Fankuchen, Division of Applied Physics, or to Professor H. Mark, Institute of Polymer Research at the Polytechnic Institute of Brooklyn, 85 Livingston Street, Brooklyn 2, New York.



Ramie

Rayon

"Amorphous" powder

X-RAY PHOTOGRAPHS

P. H. HERMANS and A. WEIDINGER

X-Ray Studies of Crystallinity of Cellulose, pages 135-144

Journal of Polymer Science Vol. IV, pp. 225-245, 1949

Dependence of Elastic Properties of Vulcanized Rubber on the Degree of Cross Linking *

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INTRODUCTION

The network-statistical theory of rubber elasticity leads to the following expression for the force of retraction in stretched rubber as a function of temperature, elongation, and network structure (1-3):

$$\tau = RT(\nu/V)(\alpha - 1/\alpha^2) \qquad (1)$$

where T is the absolute temperature, ν is the effective number of chains (3-4) extending between cross linkages within the volume V of the rubber, is the length of the stretched rubber relative to its unstretched length, and τ is expressed as the retractive force per unit initial cross-sectional area. That the contribution of the heat term, omitted from consideration in equation 1, is generally negligible has been abundantly verified by the observed proportionality between the retractive force (at constant α) and the absolute temperature (5-9). The function of α occurring in equation 1 fails to depict accurately the shape of the actual stress-strain curve, but it affords a rough approximation to it in some cases (7,8,10). Perhaps the most significant feature of the above relationship, and the one with which we are mainly concerned here, is the predicted dependence of the retractive force on the structure of the network as embodied in the factor ν/V. With rare exceptions, previous investigations on the elastic properties of vulcanized rubberlike materials have been conducted on specimens of indeterminable network structure. Hence, the validity of the proportionality between force of retraction and effective number of network elements (chains) predicted by the statistical theory of elasticity of network structures has not been subjected heretofore to experimental test.**

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*Contribution No. 154 from The Goodyear Tire and Rubber Company, Research Laboratory. Presented before the High Polymer Forum at the 112th Meeting of the American Chemical Society, New York, N. Y., September, 1947. The work presented in this paper comprises a part of a program of fundamental research on rubber and plastics being carried out under contract between the Office of Naval Research and The Goodyear Tire and Rubber Company.

**Since this paper was written, Bardwell and Winkler (10a) have published the results of an investigation dealing with the relationship of the force of retraction at 300% elongation to the degree of cross linking in vulcanized GR-S synthetic rubber samples. Vulcanization was brought about by treating GR-S latex with potassium persulfate, The effective number ν of chain elements generally depends primarily on the numbers of cross linkages introduced in the formation of the network. Conventional vulcanization of rubber with sulfur and accelerators is a complex process, and more than one type of cross linkage may be formed (11). Reliable analytical determination of the total number of cross linkages occurring in sulfur vulcanizates does not appear to be feasible at the present time.

Recently developed (12) disazodicarboxylate vulcanizing agents react quantitatively with rubber, one cross linkage being introduced for each mole of the reagent. Through the use of these compounds, rubber vulcanizates characterized by known degrees of cross linking may be readily prepared, and hitherto unexplored relationships between various physical properties and vulcanizate structure may be explored. The present investigations has been devoted primarily to the experimental determination of the dependence of the force of retraction on the degree of cross linking in rubbers vulcanized in this manner.

THEORETICAL

In order to express the "structure factor" ν/V in more tangible form, the effective number ν of chains must be related to directly measurable quantities. Consideration of the network structure leads to the relationship (3,4):

$$\nu = \nu_0 - 2N$$

where N is the number of primary molecules (i.e., polymer molecules present prior to the introduction of cross linkages) and ν_0 is half the number of cross linkages within the volume V. The indeterminate number of intramolecular "short circuit" connections should be deducted from the above expression, but otherwise it should be valid with slight approximation. Upon introducing this expression for ν into equation 1, the elasticity equation can be expressed in either of the alternate forms:

$$\tau = (RT/V_u)(\rho - 2/x)(\alpha - 1/\alpha^2) \qquad (2)$$

or:

$$\tau = (RTd/M_c)(1 - 2M_c/M)(\alpha - 1/\alpha^2) \qquad (3)$$

where ρ is the "density" of cross linked units, or fraction of the structural units which are cross linked, V_u is the volume of one unit, x is the degree of polymerization, M is the molecular weight (number average) of the primary rubber molecules, M_c is the molecular weight per cross-linked unit, and d is the density of the vulcanizate. Thus:

$$\nu_0 = \rho V/V_u = Vd/M_c$$

and the degree of cross linking was calculated from the gel-to-sol ratio. For degrees of cross linking up to 0.40 equivalent per cent ($\rho = 0.40 \times 10^{-2}$), which corresponds to the lower portion of the range investigated here, forces of retraction were observed to be several-fold greater than the predictions of equation (1). The deviation is in the same direction as we have observed, but much larger in magnitude.

and:

$$N = V/xV_u = Vd/M$$

The linear dependence of τ on the reciprocal of the primary molecular weight M at fixed α and constant density ρ of cross-linked units has been confirmed in the case of butyl rubber (4), which is particularly amenable to this type of experiment. The magnitude of the force of retraction, however, was observed to be about three times that predicted by the above theoretical equations. It was suggested that entanglements of chains may be responsible for the enhancement of $\tau_{obs.}$ as compared with the calculated value. The further suggestion was made that entanglements in butyl rubber vulcanizates may be excessive owing to the peculiar nature of vulcanization when so few reactive units are present.

The theoretically predicted influence of degree of cross linking on τ at constant primary molecular weight M is more clearly shown by equation 2. The linear relationship differs from a simple proportionality merely by the term 2/x, which can be made almost negligible by employing polymers of high molecular weight. Results on butyl rubber indicated a slower increase of τ with ρ than predicted by theory, a result which appears to be in line with the postulate that entanglements contribute appreciably to the restraints on the deformed structure. However, the range of ρ values covered in these experiments was too small for a definite decision on this point.

EXPERIMENTAL

Materials

The synthesis of the disazodicarboxylates:

$$(RO\text{-}CO\text{-}N{=}N\text{-}COO)_2R'$$

is described elsewhere (12). Decamethylene dis-methyl azodicarboxylate [10-1]* was prepared by nitric acid oxidation of the corresponding bishydrazo compound; hypochlorous acid oxidation was employed in preparing decamethylene dis-n-decylazodicarboxylate [10-10]. Both were purified by recrystallization from a mixture of ethyl acetate and hexane to constant melting points, 38-39° and 35-36°, respectively. While analytical data (12) were otherwise satisfactory, the latter [10-10] contained a trace of halogen. The 10-1 compound was stable for months at room temperature, whereas the 10-10 compound decomposed slowly on standing, the initially crystalline material changing to an oil in the course of several months. Diethylene disethylazodicarboxylate [5-2], an oil which cannot be distilled, was prepared by nitric acid oxidation of the hydrazo intermediate. Since it could not be purified, its use was restricted to preliminary explorations.

Stock solutions of natural rubber containing about 5% of rubber in benzene were prepared from pale crepe which had been subjected to slight breakdown by 15 passes between mill rolls. The solutions were prepared at room temperature, filtered with pressure and stored in the dark.

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*The numbers in brackets refer, respectively, to the number of chain atoms in the divalent radical R′ and in each of the monovalent radicals R.

GR-S synthetic rubber containing 72% butadiene was dissolved in benzene and precipitated with alcohol for the purpose of eliminating extraneous substances of low molecular weight. Approximately 1% of phenyl-β-naphthylamine was added to the precipitate before drying in vacuum at 60°. Stock solutions were prepared containing about 10% of the purified GR-S in toluene. More uniform GR-S films could be cast from this solvent than from benzene. In spite of their higher concentrations, the GR-S solutions were less viscous than the rubber stock solutions.

Concentrations of the stock solutions were accurately determined by evaporating weighed samples to dryness and weighing the residues. Intrinsic viscosities, measured on diluted portions of the stock solutions, were about 4.5 and 2.0 for the natural rubber and GR-S, respectively. These values correspond to viscosity average molecular weights of 950,000 (13) and 225,000 (14), respectively.

Preparation of Vulcanizates

A small quantity of the benzene solution containing the required amount of the disazodicarboxylate was mixed thoroughly with a weighed portion of the stock solution of rubber. The solution was subjected to vacuum for the purpose of removing gas bubbles and dissolved gases. It was then poured onto a glass tray consisting of a rectangular piece of plate glass provided around its edges with vertical barriers made of glass strips cemented to the plate glass. The tray was placed, carefully levelled, into a ventilated oven where it was heated at 60° for two hours. The vulcanized rubber sheet was then stripped from the tray. With proper manipulation, bubble-free, unrippled sheets could be obtained. Thicknesses ranged from 2 to 14 mils (inches x 10^3), depending on the quantity of rubber used. Edges of the sheets were excessively thick, but elsewhere the sheets were fairly uniform in thickness, although not accurately so.

Measurement of the Force of Retraction

Forces were measured with a triple beam balance sensitive to 0.01 g. The weighing pan was removed and a vertically adjustable platform was mounted on the base of the balance directly under the stirrup. The apparatus, exclusive of the balance, is shown diagrammatically in Figure 1. A two-inch rubber stopper A to which the lower test clamp C was fastened, was anchored, small end up, to the adjustable platform B. The rubber stopper served as the support for a 2 x 5-inch glass tube D which surrounded the sample during equilibration (see below) and measurement of the force of retraction. A thin rubber stopper E was inserted in the upper end of the glass tube. Through a small hole in the center of this stopper a fine wire F connected the upper test clamp C′ to the stirrup of the balance directly above the tube. Another hole G in the upper stopper provided for the addition and removal of equilibrating liquids.

A small dumbell test specimen was cut from the vulcanized rubber sheet using a die having dimensions similar to those described previously for microtesting of rubber (4); the mid-section is 0.100 inch wide and 0.5 inch long. A pair of ink marks H, about 1 cm. apart, was carefully placed within the uniform section of the dumbell and the ends of the dumbell were fastened in the clamps. The clamps consisted merely of pairs of aluminum plates with approximate dimensions 1.0 x 1.5 x 0.3 cm., each pair being held together by two screws. The end tab of the dumbell was held between these plates under the pressure provided by the screws.

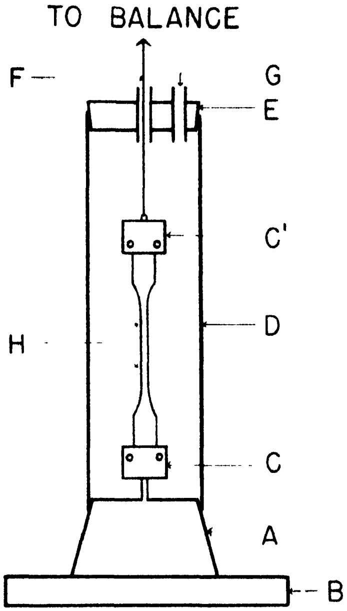

Fig. 1. Diagram of apparatus for measuring force of retraction.

After fastening the sample in the clamps, the glass tube was put in place about the sample, the wire attached to the upper clamp was inserted through the upper stopper and attached to the balance stirrup, and the upper stopper was set in place. The platform supporting the lower rubber stopper and clamp was lowered gradually until the balance reached zero position at substantially zero load on the test piece. The balance arm was locked at this point and the distance between centers of the ink marks was read with a travelling microscope reading to 0.002 inch. The platform was then lowered until the desired elongation was reached, as observed with the travelling microscope in the same manner.

The method used for equilibration is similar to that described by Gee (8).* The glass tube surrounding the test sample was filled with petroleum ether (b.p. 30-60°) and swelling allowed to proceed for about ten minutes. The petroleum ether was then removed and air or nitrogen was passed through the tube for about forty minutes to complete evaporation of all petroleum ether absorbed by the sample. The balance arm was then unlocked and the force observed. All measurements reported here were carried out at about 25°C.

*Our method of equilibration differs from that of Gee in that the sample is maintained at constant length during the swelling-deswelling cycle, whereas in Gee's experiments the sample was subjected to constant load.

The distance between the ink marks, when remeasured in several instances following the swelling cycle, was found to remain unaltered by the treatment with petroleum ether. The force, however, was appreciably less, the greater change occurring in samples of low degrees of cross linking.

Our observations confirm those of Gee pertaining to the adequacy of the above treatment for arriving at values for the force of retraction τ which are true equilibrium values characteristic of the vulcanizate network structure. Without solvent equilibration the stress continues to relax over an indefinitely long period; the value of τ arrived at in this manner is strongly dependent on the patience of the investigator. After the solvent equilibration treatment, on the other hand, the force of retraction remains constant for many hours. Typical results are shown in Table I. Even at the lowest degree of cross linking where the average distance between cross-linking points is a thousand structural units, a remarkably stable equilibrium value is secured, this value being much lower than the force observed prior to equilibration. The initial force of retraction exceeds the equilibrium value by an amount which diminishes rapidly as the degree of cross linking is increased. Thus, the equilibration operation becomes unimportant for higher values of ρ. In agreement with Gee's findings, the same equilibrium value for τ at 100% elongation was obtained when the rubber was first stretched to a higher elongation, equilibrated, allowed to retract to the chosen elongation, e.g., 100% and again equilibrated.

TABLE I. Equilibration of Natural Rubber 10-1 Vulcanizates at 100% Elongation

ρ x 100, Equiv. % of 10-1	τ before equilibration, p.s.i.	Time after equilibration treatment, hours	τ after equilibration, p.s.i.
0.10	27	0.5	14.0
		1.0	13.8
		3.	13.6
		16.	13.1
		24.	13.0
0.20	34	0.25	26.6
		1.0	26.7
1.00	85.3	0.25	83.5
		0.50	83.8
		1.25	83.7

Following the elasticity measurements, the sample was relaxed to its initial length and a 1.00-cm. segment of the mid-section of the dumbell was accurately cut out with a die. This rectangular segment, 0.254 cm. in width and 1.00 cm. long, was weighed to the nearest 0.01 mg., and the thickness and cross section were computed from the weight, assuming a density of 0.92.

Sulfur Accelerator Vulcanizates

For comparison of elastic properties, thin natural rubber sheets were vulcanized with sulfur and accelerator using the following recipe.

Pale crepe	100.	Stearic acid	1.0
Sulfur	2.5	Zinc oxide	5.0
Mercaptobenzothiazole	0.75		

Swollen Samples for Elasticity Measurements

For the purpose of exploring the influence of swelling on elastic properties of azo-vulcanized rubbers in comparison with the effect of swelling agents on rubber vulcanized with sulfur and accelerator, weighed dumbell specimens were placed in mineral oil (Nujol) for such times as were required for imbibition of the desired proportion of the swelling agent. The specimen was then removed from the mineral oil and allowed to stand overnight to assure uniform distribution throughout the sample. After reweighing, the force of retraction was measured; equilibration was unnecessary because the swelling agent assures rapid attainment of equilibrium.

Determination of Swelling Ratio. A small section (about 0.1 g.) of the vulcanized rubber sheet was weighed accurately and placed in benzene containing 1 g./liter of phenyl-β-naphthylamine. As a further precaution against degradation, swelling was carried out in darkness. Preliminary tests indicated that equilibrium was obtained within five hours.

When this point was reached, the sample was transferred to a small tube carrying a 19/38 ground glass joint. This was attached to a stopcock which was connected through a 10/30 ground joint to a T-tube. One arm of this tube led to a reservoir of benzene, the other to a vacuum pump. The system was evacuated to 20-mm. pressure and placed in a constant temperature bath at 25° for a half hour to establish equilibrium. The stopcock to the sample tube was closed, the vacuum in the remainder of the system broken, and the sample tube plus stopcock connection removed and weighed. The sample was then taken out and the tube (containing droplets of benzene) reweighed. By this procedure it was possible to obtain the weight of the swollen sample in a saturated benzene atmosphere, thus eliminating the loss of weight due to evaporation of the benzene. A blank was carried out to determine the difference in weight between the sample tube containing the benzene atmosphere and the same containing air. This correction was applied to the weight of each sample.

Five samples were measured from each vulcanizate and an average of the values was taken.

RESULTS

Preliminary Considerations

The pure disazodicarboxylates, when incorporated in rubber in the manner described above, are believed to introduce cross linkages in substantially the stoichiometric amount for reasons which may be set forth as follows:

(a) Ethyl azodicarboxylate reacts with rubber (15) and with the analogous monomeric unsaturate compound, trimethylethylene (12), giving in each case a quantitiative yield of the adduct. If an excess of either hydrocarbon is used, all nitrogen of the ethyl azodicarboxylate is combined in the adduct produced. The structure of the one-to-one adduct formed with trimethylethylene has been established (12).

(b) The 10-1 disazo compound adds quantitatively with trimethylethylene, present in excess, to form a stable adduct. This product is an oil which could not be distilled up to 300°C. at a pressure of 1 mm. Its structure has not been established but it is presumed to be analogous to the ethyl azodicarboxylate-trimethylethylene adduct.

(c) The elastic properties of the azo-vulcanized rubbers are insensitive to the temperature and time of heating, provided they are adequate for completion of the addition. The properties of vulcanizates prepared by casting films from different solvents are the same.

TABLE II. Force of Retraction as a Function of Conditions of Vulcanization[a]

Solvent	Temperature, °C.	Time, hours	τ, at 100% elongation, p.s.i.
Benzene	60	2	48.9
Benzene	60	2	50.7
Benzene	60	2.5	47.1
Benzene	60	3	50.9
Benzene	60	3.5	51.1
Toluene	60	2	50.4
Carbon tetrachloride	60	2	50.2
Benzene	40	3	64.4[b]
Benzene	70	1.5	66.0[b]

[a] All natural rubber vulcanizates prepared using 1.0 equivalent per cent of 5-2 .

[b] A different, apparently purer, preparation of the 5-2 equivalent compound was used in these two experiments.

Preliminary results such as those shown in Table II indicated the adequacy of two hours at 60° for completion of the addition reaction. Different preparations of the 5-2 disazo-vulcanizing agent used in these experiments gave discordant results owing to the variable purity of this compound. Sets of results obtained by using the same batch of vulcanizing agent provide the necessary information, however. Further use of the 5-2 compound was abandoned in favor of the 10-1 and 10-10 compounds which may be obtained in crystalline form. Similar, though less complete, exploratory experiments demonstrated that 2 hours at 60° was also sufficient for vulcanization with the 10-1 compound. It was found further that films prepared by casting a solution of natural rubber and 10-1 in the low-boiling solvent, ethyl bromide, followed by heating for 1 hour or more at 60° exhibited tensile strengths and ultimate elongations agreeing closely with values obtained using benzene as solvent. GR-S reacted with the azo compounds at a similar rate.

It would be difficult, if not impossible, to demonstrate in a straightforward manner by any presently known technique whether or not chain scission accompanies the cross-linking process. That the primary rubber molecules survive the azo-vulcanizing process without excessive degradation is indicated, however, by the rather small change in intrinsic viscosity occurring when rubber films are prepared according to the standard procedure using small proportions of ethyl azodicarboxylate in place of the disazo compound. These results are shown in Table III. The rather marked decrease in intrinsic viscosity when larger proportions are used must be caused, in part at least, by the chemical modification of the polymer chain resulting from formation of the adduct. Benzene is a poor solvent for the modified rubber chains, hence the intrinsic viscosity is diminished on this account. The molecular weight values for the more highly modified rubbers included in Table III may be considerably too low for this reason.

TABLE III. Effects of Ethyl Azodicarboxylate (EAD) Addition on the Intrinsic Viscosity of Natural Rubber[a, b]

Equiv. % of EAD	Intrinsic viscosity in benzene	$\overline{M}_v \times 10^{-5}$ calculated[c]
0	5.09	10
2	4.70	9.2
4	2.96	4.6
8	2.92	4.5

[a] All films cast from benzene solutions containing EAD, then dried at 60° for 2 hours.

[b] The intrinsic viscosity of the rubber in the stock solution was 5.26.

[c] The viscosity average molecular weight values given in the last column are viscosity averages calculated from the relationship of Carter, Scott, and Magat (13) for rubber in toluene; intrinsic viscosities for rubber in benzene and in toluene are similar.

Effect of Sample Thickness

The retractive force per unit cross-section at a given elongation was observed to vary somewhat with the thickness of the sheet, as shown by the results plotted in Figure 2. The effect appears to vanish for low proportions of the vulcanizing agent, and with higher proportions it becomes small, below a thickness of about 5 mils. Sulfur vulcanizates exhibited τ values independent of thickness. Four rubber sheets varying from 12 to 25 mils in thickness but otherwise identically prepared by vulcanizing in a press for 30 minutes at 285°F.

using the sulfur-mercaptobenzothiazole recipe given above registered identical values for τ at 100% elongation.

The possibility that the above behavior of the azo vulcanizates is related to the occurrence of partial vulcanization prior to evaporation of solvent appears to be ruled out by the uniformity of results obtained with different solvents (see below). We are inclined to attribute the observed dependence of properties on thickness to the limited compatibility of the disazo-vulcanizing agents with rubber; when the proportion of the azo compound is large, it may tend to segregate (although not visibly so) on the surface and, if the sheet is thick, diffusion may be too slow to assure uniform reaction throughout. On the other hand, an appreciably "tighter cure" on one surface than on the other is rendered unlikely by the observation that samples swollen in solvents show no tendency to curl.

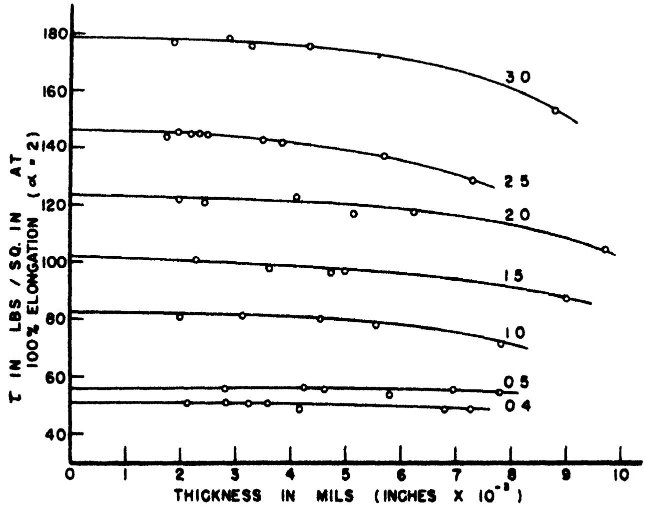

Fig. 2. Force of retraction τ vs. thickness of vulcanized sheets for the various proportions of 10-1 vulcanizing agent indicated by the equivalent percentage figures ($\rho \times 100$) adjacent to each curve.

Whatever may be the cause of the variation in elastic properties with thickness, the magnitude of the effect is not large and approximately constant values for τ are observed for all thicknesses below 5 mils. Extrapolation to zero thickness offered the best means for minimizing the influence of the anomaly.

The Stress-Strain Relationship

The stress in conventionally vulcanized rubber is known to depend on the relative length α in a manner which is approximated only roughly by the function of α occurring in the alternate equations 1-3 derived from the network-statistical theory of rubber elasticity(3,7,8, 10). The departure of the stress dependence on elongation from theory has been shown in a particularly effective manner by Gee (8) who calculates a quantity designated as χ which is proportional to the ratio of the observed force of retraction $\tau_{obs.}$ to that calculated from equation 1. Modifying equation 1 to include networks swollen with diluent after vulcanization:

$$\tau = RT(\nu/V)(\alpha - 1/\alpha^2)/v_2^{1/3} \qquad (4)$$

where α is ratio of the length of the stretched, swollen sample to unstretched, swollen length and v_2 is the volume fraction of polymer (rubber) in the swollen sample. Then χ is defined by Gee as follows:

$$\begin{aligned}\chi &= (\tau_{obs.}/\tau_{calcd.})(V/R\nu) \\ &= \tau_{obs.}/[T(\alpha - 1/\alpha^2)/v_2^{1/3}]\end{aligned} \qquad (5)$$

Whereas, according to theory, χ should be a constant for a given vulcanizate, Gee observed that it decreased with increase in α in all cases investigated, including gum vulcanizates of various synthetic rubbers as well as natural rubber. He also showed that χ tends to decrease on swelling, the change in χ with α for swollen rubbers being small.

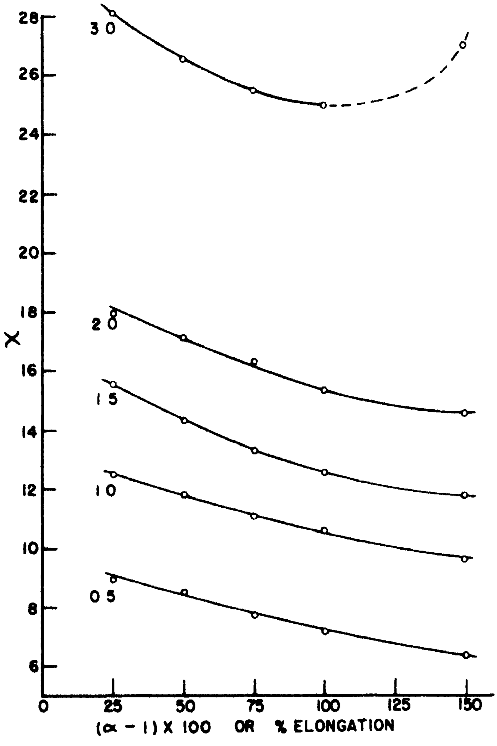

Fig. 3. Relative stress dependence on elongation. χ, representing a quantity proportional to $\tau_{obs.}/\tau_{calcd.}$, plotted against the relative extension α for the degrees of cross linking ($\rho \times 100$) indicated with each curve.

In Fig. 3 the magnitude of the variation of χ with α for azo-vulcanized rubbers is seen to be roughly independent of the extent of cross linking. Considered from the standpoint of the percentage variation of χ with α, the effect is relatively unimportant at high degrees of cross linking but excessively so at very low degrees. When ρ = 0.10, for example (results not shown in Fig. 3), the effect is manifested by an increase of only about 10% in τ between α = 2 and 3. At high degrees of cross linking the data suggest that χ passes through a minimum value beyond which it increases with further elongation.

The effects of a diluent (Nujol) on χ, shown in Figures 4 and 5, parallel the observations of Gee on sulfur vulcanizates. The displacement of χ_2 with addition of diluent seems to be greater for the $\rho = 1.00 \times 10^{-2}$ azo vulcanizate than for the sulfur-accelerator vulcanizate (30 minute cure at 285°F.) shown for comparison. The results obtained for somewhat higher degrees of cross linking ($\rho = 1.5$ and 2.0×10^{-2}) exhibit a smaller change of χ with swelling, which is more in line with the sulfur vulcanizate results. The conclusion appears justified that the elastic properties of the azo vulcanizates do not differ significantly from those of rubbers vulcanized in the conventional manner to similar degrees of cross linking.

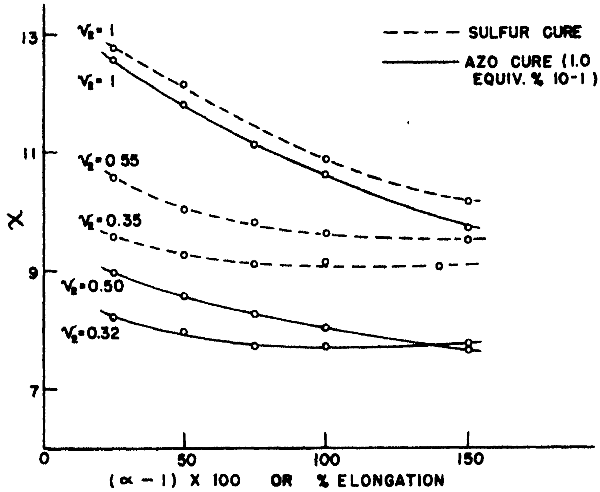

Fig. 4. Relative stress dependence on elongation for azo- and for sulfur-vulcanized natural rubber swollen to the various degrees indicated for each curve. (Swelling-volume ratio = $1/v_2$.)

The cause of the deviation of $\tau_{obs.}$ from its theoretically predicted dependence on ρ and degree of swelling ($1/v_2$), as demonstrated by the variation in χ , is not clear. As Gee pointed out, the swollen rubbers behave more nearly in accordance with theory than the unswollen rubbers, and χ for the latter at higher elongations approaches the fairly constant value assumed by χ for the highly swollen samples. These observations led Gee (8) to conclude that a swollen and/or stretched ($\alpha \cong 2$) rubber behaves approximately "ideally" and that the unswollen vulcanizate at low elongation deviates most widely from "ideality." Gee's suggestion that this deviation is caused by a tendency for the rubber chains to assume a condition of alignment, this tendency being enhanced by elongation and depressed by swelling, is untenable from either of two points of view. On purely thermodynamic grounds, no system will spontaneously tend toward a more ordered state unless this state offers a lowering of internal energy. Thermoelastic measurements, however, show that the internal energy of the rubber is very nearly independent of the elongation. Secondly, if Gee's explanation were correct, the anomaly in χ would surely be widely variable among various types of rubbers. Gee's results show that this is not the case.

Pasternak and Kuhn (16) recently observed that the elastic modulus of vulcanized rubber at small extensions decrease more rapidly with swelling than theory would predict. This observation is equivalent to the decrease in χ discussed above for somewhat greater extensions. They attributed the deviation from theory to secondary bonds between chains, these bonds acting to increase the degree of cross linking in the unswollen rubber, but being broken in the presence of the swelling agent. This conclusion appears to be untenable inasmuch as equilibration by temporarily swelling the unswollen samples in the above manner does not eliminate the discrepancy between χ values for the swollen and unswollen samples.

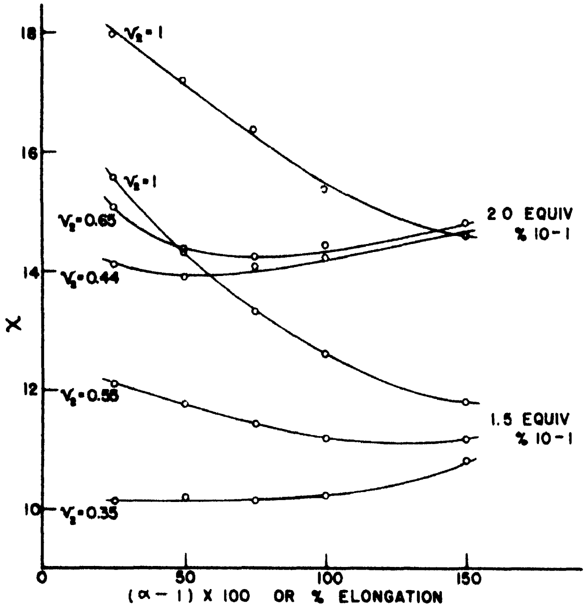

Fig. 5. Relative stress dependence on elongation for higher azo vulcanizates swollen to the various degrees indicated.

It should be kept in mind that the derivation of the equation of state for rubber rests on a number of assumptions and approximations. Of these, the use of the Gaussian distribution function to represent both relative numbers of configurations and the chain displacement length distribution, and the disregard of the random lengths of the chain elements, would seem to be of likely significance in connection with the stress-strain behavior considered above. A minor deviation of the actual probability distribution of chain lengths from the Gaussian form would lead to "anomalies" of the magnitude observed above. These remarks are in no wise considered to offer an explanation of the observations; they are intended merely to emphasize the importance of avoiding a too-literal acceptance of the predictions of network-statistical theory, particularly in regard to the precise form of the stress-strain relationship.

Dependence of the Force of Retraction on the Degree of Cross Linking

The results and discussion of the last section leave unanswered the question as to what elongation (and degree of swelling) should be chosen for comparing the forces of retraction in rubbers cross linked to various degrees. According to results shown in Figures 3-5, the shape of the τ vs. ρ curve at a given elongation will be appreciably dependent, particularly at low values of ρ, on the choice of elongation; the lower part of the curve (near $\rho = 0.2 \times 10^{-2}$) may be altered as much as 50% relative to the upper (high ρ) end of the curve, depending on the elongation at which the comparisons are made.

Somewhat arbitrarily, but in part for the sake of experimental convenience, we have chosen 100% elongation ($\alpha = 2$) for this purpose. Results obtained with natural rubber vulcanizates prepared using various proportions of the 10-1 disazo compound are shown in Table IV. Most of the values represent extrapolations to zero thickness from the results shown in Figure 2. There extrapolation was not employed, the proportions of vulcanizing agent for the first two samples are small enough to obviate the need for extrapolation.

TABLE IV. Force of Retraction at 100% Elongation and Degree of Cross Linking; Natural Rubber Vulcanized with 10-1

Equiv. % of 10-1, $\rho \times 100$	Sheet thickness, mils	τ, p.s.i.
0.10	16.5	13.5
0.20	11.0	26.7
0.40	Extrapolated to zero	50
0.50	Extrapolated to zero	55
0.80	9.6	69
1.00	Extrapolated to zero	82
1.50	Extrapolated to zero	102
2.00	Extrapolated to zero	124
2.50	Extrapolated to zero	147
3.00	Extrapolated to zero	178

These characteristic τ values for $\alpha = 2$ are plotted against ρ in Figure 6. The broken straight line represents the theoretical relation according to equation 2, assuming $2/x = 0$. The actual value of x (number average) may be assumed to be least 5000. Hence x/2 is all but negligible in equation 2, and the required displacement of the intercept of the theoretical line from the origin in Figure 6 should be barely perceptible. Also included in Figure 6 are average τ values for rubber vulcanizates prepared by using the 10-10 disazo compound. The results on which these averages are based were erratic, presumably due to the instability of our sample of this vulcanizing agent. The accuracy of this set of points is therefore questionable and no significance is attached to the fact that they are in general somewhat higher than the much more reliable values for the 10-1 vulcanizates.* Over most of the range, τ for a given proportion of cross-linking agent, appears to be approximately independent of the particular agent selected.

Observed magnitudes for τ on the whole are remarkably close to the predictions of theory. The change in τ with ρ is less than predicted, however, τ being higher than theory for low degrees of cross-linking, while the reverse is true at high degrees. The nature of the variation of χ with α (Fig. 3) makes clear that this deviation could not be appreciably reduced by choice of an α other than 2 for the force measurements; if a lower α were chosen, this deviation would be enhanced somewhat.

Corresponding results on the dependence of τ at $\alpha = 2$ on ρ for GR-S vulcanized with 10-1 are given in Table V and Figure 7. ρ is expressed in equivalents per butadiene unit. In most cases the values represent measurements at low thickness without extrapolation to zero thickness. The theoretical line has been drawn according to equation 2 again neglecting 2/x. Although the number average x (representing the number of butadiene units per molecule) for the precipitated GR-S used in these experiments is unknown, it probably is of the order of 1000 and 2/x is not negligible. The theoretical straight line should be shifted to the right by an uncertain amount, presumed to be of the order of 0.2×10^{-2} unit in ρ.

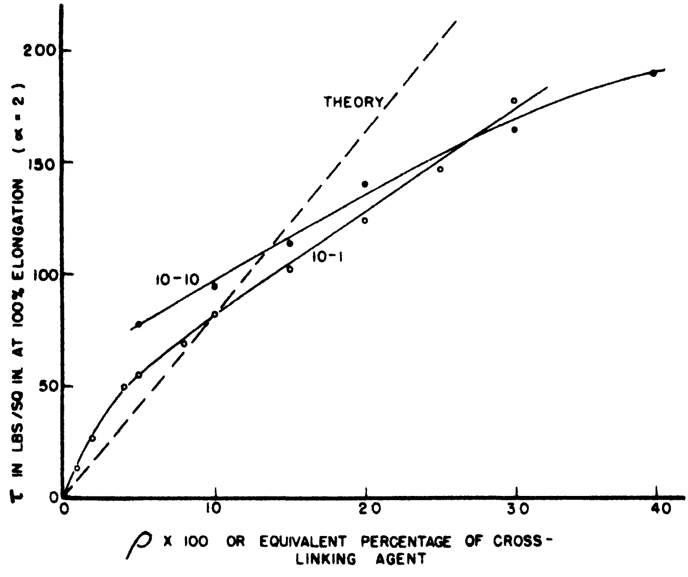

Fig. 6. Dependence of the force of retraction on degree of cross linking for natural rubber vulcanizates.

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*Since the 10-10 preparation proved to be unstable, it may have undergone appreciable decomposition during the vulcanization operation. In analogy with decompositions of other azo compounds, free radicals doubtless are released and these may, depending on the circumstances, lead to larger extents of interlinking than would have been realized by the addition reaction alone. The larger τ values obtained with 10-10 as compared with 10-1 may be accounted for in this manner.

TABLE V. Force of Retraction at 100% Elongation and Degree of Cross Linking; GR-S Vulcanized with 10-1

Equiv. % of 10-1, ρ x 100	Sheet thickness, mils	τ, p.s.i.	τ Average
0.50	3.81	61.3	
	3.81	61.1	61.4
	3.67	61.7	
1.0	6.02	83.1	
	5.04	83.6	83.2
	7.10	83.0	
1.5	5.91	121.0	
	4.34	123.0	121.8
	3.97	121.3	
2.0	6.01	147.9	
	5.80	147.9	148.0
	6.07	148.1	
2.5	5.27	159.9	
	5.69	158.2	160.0
	5.07	161.9	

The results for GR-S agree with the theory somewhat better than is the case for the natural rubber vulcanizates. The same type of deviation is apparent, however.

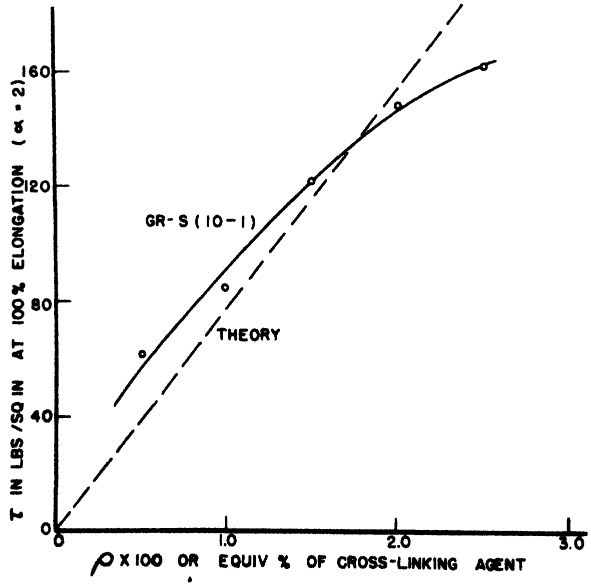

Fig. 7. Dependence of the force of retraction on degree of cross linking for GR-S vulcanizates.

Equilibrium Swelling

Force of retraction measurements at 100% elongation could not be extended satisfactorily beyond $\rho = 3 \times 10^{-2}$ owing to the tendency of more highly cross-linked samples to tear at the test clamps.

TABLE VI. Equilibrium Swelling of Natural Rubber 10-1 Vulcanizates in Benzene at 25°C.

$\rho \times 10^2$	SV = $1/v_2$	$\tau_{obs.}$ at 100% elong., p.s.i.	τ[a] at 100% elong. calcd. from swelling	τ[b] at 100% elong. calcd. from theory
0.50	5.89	55	58	42
1.00	5.11	82	82	83
2.00	4.27	124	128	161
3.00	3.88	178	163	235
4.00	3.66		190	305
6.00	3.40		230	435
10.0	2.87		370	660
20.0	2.31		700	1070
30.0	1.94		1280	1360
40.0	1.71		1860	1560

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[a] Calculated from equilibrium swelling volume ratio ($1/v_2$) using equation 7 with μ_1 = 0.430 and for α = 2.

[b] Calculated from elasticity theory according to equation 8.

Response of the vulcanizate structure to deformation may also be adduced from equilibrium swelling measurements, which may be extended to considerably higher degrees of cross linking. Results of such measurements carried out in benzene on samples for which $\rho \times 10^2$ varied from 0.5 to 40 are recorded in Table VI. In Figure 8 the swelling-volume ratio SV $= 1/v_2$, representing the ratio of the volume of the swollen sample at equilibrium to its unswollen volume, is plotted against ρ over the range 0.5 to 20 x 10^{-2}.

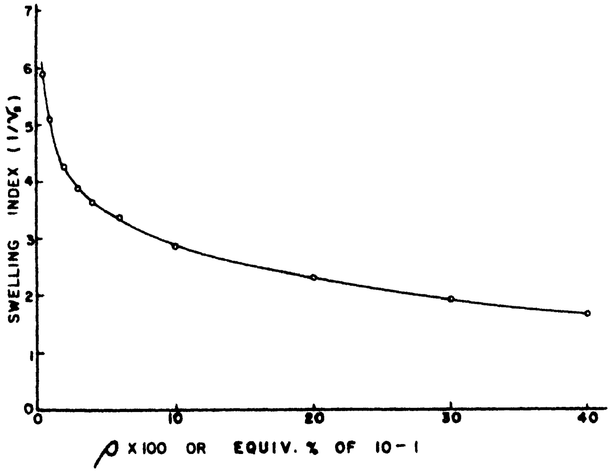

Fig. 8. Swelling-volume ratio (SV = $1/v_2$) vs. degree of cross linking for natural rubber in benzene at 25°C.

According to the statistical mechanical treatment of swelling (17,18), at equilibrium:

$$-[\ln(1-v_2)+v_2+\mu_1 v_2^2]/(v_2^{1/3}-v_2/2) = (\nu/V)V_1 \qquad (6)$$

where V_1 is the molar volume of the solvent and μ_1 is the energy of interaction parameter equal to BV_1/RT where B is the cohesive energy density constant for the polymer-solvent pair.* Substituting for ν/V from equation 1:

$$-[\ln(1-v_2)+v_2+\mu_1 v_2^2]/(v_2^{1/3}-v_2/2) = [\tau/(\alpha-1/\alpha^2)](V_1/RT) \qquad (7)$$

which relates τ and v_2 independent of the vulcanizate network structure. Both τ and v_2 have been determined for each of the four lowest vulcanizates listed in Table VI. Hence, it is possible to calculate apparent values of μ_1 for each of these samples as follows: 0.438, 0.431, 0.435, and 0.415. Although application of the same μ_1 value over the entire range is questionable, equivalent values of τ have been calculated from v_2 using the average $\mu_1 = 0.430$. These are given in the fourth column of Table VI where they may be compared with the observed τ's given in the third column and with those in the last column calculated from the degree of cross linking according to theory. The alternate equation 3 has been used for this purpose, neglecting the inconsequential $2M_c/M$ term and making allowance for the relatively large weight fraction of the vulcanizing agent in the higher vulcanizates through the use of the relationship:

$$M_c = 68/\rho + 402/2$$

where 402 represents the molecular weight of the 10-1 disazo compound. Assuming the same density, 0.92, for all vulcanizates:

$$\tau_{\alpha=2} = 5.8 \times 10^6/(201 + 68/\rho) \qquad (8)$$

from which figures in the last column of Table VI have been calculated.

The τ's computed from the swelling measurements (column four) may deviate appreciably from the actual forces of retraction which, if measureable, would be exhibited by the higher vulcanizates. A moderate decrease in μ_1 with increase in ρ in the intermediate range is indicated. This would lead to somewhat larger values for the τ's calculated from swelling in this range. At the highest degrees of cross linking, μ_1 must increase owing to the increasing polar character of the polymer resulting from the large percentage of azodicarboxylate content. The τ's calculated from swelling data on the last two or three samples may for this reason be much too large, hence comparisons here may be of little significance. In spite of these limitations, the data in Table VI serve to show that the force of retraction continues to increase with ρ over a much wider range than was ascertainable from direct measurement of τ.

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*Equation 6 differs slightly from the previously published swelling equation (17) by the inclusion of $-v_2/2$ in the denominator term. Its effect is not large provided that v_2 is small. The deviation of this preferred relationship will be published elsewhere.

CONCLUSIONS

The results reported above demonstrate a progressive increase in the force of retraction τ at fixed elongation with increase in the fraction ρ of the structural units which are cross linked from $\rho = 0.10 \times 10^{-2}$ to 3.0×10^{-2}. Over this range, τ at 100% elongation increases about thirteenfold. Swelling measurements indicate that the increase in τ with ρ continues over an additional tenfold range in ρ. Previous assertions (19) that the modulus of elasticity of soft gum rubber vulcanizates depends largely on chain interaction and entanglements other than those imposed by the cross linkages, and that the modulus therefore is not directly related to the degree of cross linking, are without foundation.

The statistical theory of rubber elasticity expresses the force of retraction as a function of the temperature, vulcanizate structure and elongation; no arbitrary constants are involved. The magnitudes of τ for $\alpha = 2$ are in remarkably close agreement with the predictions of the theory over most of the range in ρ. This fact is of the utmost significance in confirmation of the statistical theory of rubber elasticity and of the analysis of the network structure of vulcanized rubber.

On the other hand, τ increases less rapidly with ρ than the direct proportionality prescribed by theory. Forces of retraction are higher than the theory predicts at low degrees of cross linking, and an opposite deviation is observed for values of ρ greater than about 1×10^{-2}. Previous observations on butyl rubber (4), vulcanized to ρ values from about 0.16×10^{-2} to 0.28×10^{-2} indicated forces of retraction (for infinite molecular weight M) which exceed by about threefold those predicted from the theory. This deviation is decidedly larger than has been observed here in the same range for ρ. A substantial part of the discrepancy observed for butyl rubber may have arisen from failure to secure elastic equilibrium, however.

Deviations in the values of τ from theory probably originate largely from over-simplifications in the treatment of the network structure. Entanglements of the sort previously discussed (3,4) tend to enhance the restraints imposed on the chains when the rubber is elongated. Their percentage effect should be greatest for low degrees of cross linking, hence the observed τ's are higher than theory at low degrees of cross linking. "Intra-molecular" cross linkages, yielding short-circuit structures contributing nothing to the elastic reaction of the network, should become increasingly important at higher degrees of cross linking (3,4). Such wastage of cross linkages may account for the low values of τ obtained for higher ρ's.

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Synopsis

Natural rubber and GR-S synthetic rubber have been vulcanized to varying degrees of cross linking through the use of disazodicarboxylates. These compounds react readily with the above unsaturated polymers in a manner which assures the formation of one cross linkage for each molecule of the disazo compound. Elastic properties of the vulcanizates so produced are similar to those of rubber specimens vulcanized in the conventional manner with sulfur and an accelerator. Their stress-strain curves deviate from the form prescribed by the statistical theory of rubber elasticity in the same manner as observed by Gee for sulfur vulcanizates. The equilibrium force of retraction at 100% elongation has been measured over a 30-fold range in the degree of cross linking; equilibrium swelling measurements extend over an 80-fold range. The magnitude of the force of retraction over most of the range covered agrees remarkably well with the explicit predictions of the statistical theory. The significance of the deviations which are observed is discussed.

Résumé

Des échantillons de caoutchouc naturel et synthétique (GR-S) ont été vulcanisés à différents degrés de pontage, par l'utilisation de disazodicarboxylates. Ces composés réagissent facilement avec les polymères non-saturés, cités ci-dessus, de telle façon qu'il se forme

un pontage pour chaque molécule de composé disazoïque. Les propriétés élastiques des vulcanisats ainsi obtenus sont semblables à ceux des échantillons de caoutchouc, vulcanisés de la façon habituelle avec du soufre et un accélérateur. Leurs courbes tension-élongation dévient de la forme prévue par la théorie statistique de l'élasticité des caoutchouc, de la même manière que pour les vulcanisats au soufre, tel que l'a observé Gee. La force d'équilibre de contraction à 100% d'élongation a été mesurée dans des variations du degré de pontage, variant de un à 30 fois sa valeur. L'équilibre de gonflement a été mesuré sur une série dont le degré de pontage variait jusqu' à 80 fois. La grandeur de la force de contraction pour tous ces échantillons s'accorde remarquablement bien avec les prévisions explicites de la théorie statistique. La signification des écarts observés est discutée.

Zusammenfassung

Naturgummi und Buna-S-artiger Kunstgummi wird durch Anwendung von Disazodicarboxylaten bis zu verschiedenen Vernetzungsgraden vulkanisiert. Diese Verbindungen reagieren leicht mit den ungesattigten Polymeren in einer Weise, die die Bildung einer Vernetzung für jedes Molekül der Disazoverbindung sicherstellt. Die elastischen Eigenschaften der auf diese Weise hergestellten Vulkanisate sind ahnlich der von Gummiproben, die mit Schwefel und einem Beschleuniger konventionell vulkanisiert wurden. Ihre Belastungskurven weichen von den durch die statistische Theorie der Gummielastizität gegebenen in derselben Weise wie von Gee für Schwefelvulkanisate beobachtet wurde, ab. Die Gleichgewicht-Rueckzieh-kraft bei 100% Dehnung wurde über einen dreissigfachen Bereich des Vernetzungsgrades gemessen. Gleichgewichts-Quellungsmessungen umfangen einen 80-fachen Bereich. Die Grösse der Rückziehkraft stimmt im Grossteile dieses Bereichs bemerkenswert gut mit den Voraussagen der statistischen Theorie überein. Die Bedeutung der Abweichungen, die beobachtet wurden, wird erörtert.

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Investigations on Cellulose Nitrate. II. Liquid and Vapor Phase Adsorption of Acetone*

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In interpreting the results of investigations of the behavior of polymer molecules in solution (e.g., sedimentation or diffusion), it is of importance to know something of the nature and extent of the interaction of the polymer molecules with the surrounding solvent molecules. There are two extreme possibilities:

(1) Each polymer molecule is associated with a definite quantity of solvent so tightly bound that it must be considered as part of the polymer kinetic unit in solution.

(2) The polymer and solvent are inert toward each other, collisions between them resulting in only extremely transient encounters.

More probable than such extremes, however, is some intermediate state in which, although solvent-polymer interaction is by no means negligible, it cannot be considered permanent. A quantitative estimate of these intermediate states for different systems is clearly fundamental, but, as yet, information on such questions is very meager. Available estimates have, in the main, been based upon x-ray measurements, upon results of adsorption*** measurements in the presence of organic materials (usually of a ketonic or ester type), and upon corresponding thermochemical measurements. Trogus, Tomonari, and Hess (1) studied refractometrically the adsorption of acetone and other ketones by cellulose nitrate (nitrogen content = 13.6%) from ketone-ligroin mixtures, and stated that limited acetone adsorption occurred, the higher acetone concentrations giving no increased adsorption. The limiting value was stated to correspond to three molecules of acetone per glucose residue, and, in conjunction with corresponding x-ray measurements, the work was considered strong evidence for the existence of a compound between acetone and cellulose nitrate. Kargin and Papkov (2) carried out similar refractometric studies on the adsorption by cellulose nitrate of acetone from mixtures with petroleum ether and also concluded that limited adsorption occurred. The latter workers further measured heats of adsorption and, assuming that the partial heat of adsorption did not vary with the degree of adsorption, calculated from the total heat of solution the extent of adsorption by cellulose nitrate in solution. They thus deduced that, in solution, one molecule of acetone was associated with each nitrate group, and considered this result to be evidence of the formation of an addition compound. It has, however, more recently been shown by Calvet (3) that the partial heat of adsorption varies considerably with the degree of adsorption, so that Kargin and Papkov's treatment of thermochemical results is not tenable. More recently the adsorption of acetone from mixtures with hexane and cyclohexane has been studied by Petitpas (4), but no well defined limiting adsorption was reported in this work.

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***The term "adsorption" is used throughout to indicate the process by which acetone is taken up by cellulose nitrate. It should not, however, be inferred that surface forces alone are responsible for this uptake.

The adsorption by cellulose nitrate of acetone from the vapor phase has been studied by several workers: (McBain and co-workers (5); Rubenstein (6); Desmaroux (7); Jenkins and Bennett (8); Matthieu (9); and Petitpas (4)); all of whom are in agreement that the isotherm is quite continuous, no signs of limiting adsorption occurring. Infinite adsorption is approached as the activity of acetone approaches unity.

Clearly, if acetone is mixed with a liquid which is truly inert to the cellulose nitrate, the acetone uptake at any acetone activity should be identical with that from the vapor phase at the same activity. The limited adsorption from acetone-liquid mixtures reported by several workers is incompatible with the continuous vapor phase isotherms and needs explaining.

Several authors have also observed the effect of the adsorption of acetone and other liquids on the x-ray diagram of cellulose nitrate, although not all agree on the interpretation of the results. Trillat (10) cast films of cellulose nitrate from solution in acetone and other solvents and took x-ray photographs at different stages of the removal of the solvent. Solvent-free films showed a prominent spacing of 7.2 A. whatever the solvent used in casting the film, but, in the early stages of the removal of the solvent from newly cast films, considerably larger spacings were observed, the 7.2 A. spacing being simultaneously reduced in intensity. For instance, after heating a film cast from acetone solution for 15 minutes at 70°C. (the shortest drying time which could be used), the maximum spacing observed was 15.1 A. another at 9.7 A. also existing clearly. Subsequent experiments on the effect of stretching on the x-ray diagram of films showed that the larger spacing corresponded to an interchain distance approximately perpendicular to the chain axis. Since the x-ray examination of the film could be made only when the latter had sufficient mechanical strength to be removed from its support and handled, it is not improbable that the 15.1 A. spacing is by no means the maximum interchain spacing in a highly solvated film. Trillat attributes the changed character of the cellulose nitrate diagram on adsorption of acetone to combination by addition. Trogus, Tomonari, and Hess (1) also examined cellulose nitrate by x-rays after acetone adsorption from liquid mixtures and, in view of the changed diagrams obtained and of the adsorption results already quoted, concluded that compounds between the polymer and acetone occurred which could dissolve in the excess acetone. On the other hand, Matthieu (9), and Desmaroux and Matthieu (11), on the basis of acetone adsorption from the vapor phase and the continuously varying x-ray diagram obtained from cellulose nitrate with varying acetone content, considered that the interaction was in the nature of a solid solution rather than the compound formation favored by Hess and co-workers. Petitpas (4), who later continued the study by x-rays of the adsorption of acetone and other organic liquids by cellulose nitrate fibers, had a similar view of the nature of the interaction.

Among thermochemical studies on cellulose nitrate that of Calvet and his collaborators (3) is of great interest. At low acetone adsorption for cellulose nitrates of 11.5% and 14% nitrogen content, the partial heat of adsorption is positive and constant until about 3 molecules of acetone per glucose unit are adsorbed. With increasing adsorption, the partial heat of adsorption for the cellulose nitrate of lower nitrogen content decreases regularly, until at a point corresponding to 6 acetone molecules per glucose unit, there is an abrupt change, which appears (according to Calvet) to indicate the formation of a complex "cellulose nitrate acetonate." No special interest attaches to the points: (a) 1 molecule of acetone per glucose unit; and (b) 1 molecule of acetone per nitrate group.

It would therefore appear that thermochemical support is not forthcoming for the existence of the cellulose nitrate compounds postulated from adsorption and x-ray studies.

Summarizing, there appear to be two main contradictions:

(a) The adsorption isotherms for a given substance from the liquid (mixed with an inert solvent) and vapor phases are different.

(b) Experimental data has been variously interpreted as indicating both compound formation between cellulose nitrate and acetone (or other ketones), and the formation of solid solutions to the exclusion of compound formation.

Before presenting new experimental data on these two apparent contradictions, the following comments should be made:

(1) An adsorption from liquid mixtures different in character from the vapor adsorption might readily be explained as arising from the fact that the second liquid component is not completely inert to the polymer, as suggested by Petitpas (4). According to the particular system, this might cause increased or decreased adsorption of the main component.

(2) It would appear that the presence of new, larger spacings in solvated films cannot by itself be taken as proof of the existence of solvent-polymer compounds. The mere retention of solvents in non-stoichiometric proportions by dipolar interactions or other secondary forces could lead to increased interchain spacings of the type observed. It seems likely that some of the difficulties arise from a certain looseness in using the term "compound" to describe the products of interaction of cellulose nitrate and acetone. In the strict sense of the term, a compound must not only contain its constituents in stoichiometric proportions, but must also possess considerably stability. Energetically, this involves the existence of an energy of activation for the dissociation which is considerably greater than the thermal energy of the molecules and the energy involved in intermolecular collisions. In the absence of information of this type, it is scarcely justifiable to speak of compounds of cellulose nitrate and acetone.

The experimental investigations on the adsorption of acetone by cellulose nitrate are considered in three sections: (1) isotherms from the vapor phase; (2) isotherms from the liquid phase; and (3) comparison of vapor and liquid phase isotherms.

ADSORPTION FROM THE VAPOR PHASE

The vapor phase adsorption isotherms were obtained by weighing the cellulose nitrate and the acetone adsorbed at a given vapor pressure by means of a McBain and Baker (12) adsorption balance, in which the extension of a quartz spring, observed by a travelling microscope, was used to measure the weight directly. This method eliminates any errors due to absorption of acetone on other parts of the apparatus, such as greased stopcocks. About 0.25 g. cellulose nitrate was used, and an adsorption of 0.00005 g. acetone could be measured. The vessel in which the adsorption balance was hung was thermostatted to ±0.01°C. The remainder of the apparatus was kept at a temperature about 5°C. above that of the thermostat to prevent acetone condensing out. The whole apparatus could be evacuated by a mercury diffusion pump. Acetone, which had been dried over anhydrous potassium carbonate and then distilled, was degassed and fractionated under vacuum conditions, only the middle third being used. After being placed in the apparatus, the cellulose nitrate was evacuated for at least 24 hours, although there was generally no detectable change in weight over 30 minutes.

Sufficient acetone vapor was allowed to enter the adsorption vessel and the uptake of acetone was measured at intervals until equilibrium was reached. The time required depended upon the physical state of the sample of cellulose nitrate but was never more than 10 hours. This procedure was repeated with further doses of acetone. Points on the isotherm during desorption were obtained by a similar procedure after removing some acetone by condensing it outside the adsorption vessel.

Isotherms for adsorption and desorption are given in Figure 1 and are the same within the limits of experimental error. This agreement could only be obtained if the desorption was carried out extremely slowly. If the acetone pressure were rapidly decreased, a pseudo-equilibrium state (e.g., point A of Figure 1) was reached which showed no decrease in the quantity of acetone adsorbed at constant acetone pressure over a period of 5 days. When removed from the apparatus, the complex of cellulose nitrate and acetone consisted of a hard, horny outside layer while the inside was still a soft gel containing considerable acetone. It appears, therefore, that the large values of adsorbed acetone obtained during rapid desorption are not true equilibria but are due to the production of a hard, coherent surface structure through which acetone diffuses only extremely slowly.

The isotherms (Fig. 1) for a fiber and a reprecipitated cellulose nitrate are identical, which shows that they do not depend upon the physical state and hence upon the crystalline-amorphous ratio of the cellulose nitrate. It would appear, therefore, that acetone must react with individual cellulose nitrate molecules, rather than merely with the external surface of crystallites or micelles.

Many authors, including Jenkins and Bennett (8), have shown that the uptake of acetone by cellulose nitrate is virtually independent of its average molecular weight (as measured by the specific viscosity) up to about 10 moles of acetone per glucose residue, but there is not such complete agreement about the effect of the nitrogen content on adsorption. Jenkins and Bennet (8) and Rubenstein (6) measured the gas phase adsorption at one activity only for cellulose nitrates of nitrogen contents above 10% and found that there was some variation, a maximum occurring at about 12% nitrogen content. On the other hand, Desmaroux (7) and, more recently, Petitpas (4) determining complete isotherms, have shown that these are identical for cellulose nitrates with two and three nitrate groups per glucose residue. These results are not necessarily contradictory, since, if there is a maximum, cellulose nitrates of different nitrogen contents may have similar isotherms. Gas phase isotherms for a wide range of nitrogen contents are given in Figure 2. The adsorption of acetone is limited in extent for the cellulose nitrate of 5.3% nitrogen content, which is insoluble in acetone, and, possibly— at a much larger molar ratio of acetone to glucose residues—for the cellulose nitrate of 10.1% nitrogen content, which is also not completely soluble. There was no limit to the adsorption of acetone by the other cellulose nitrates, and their isotherms showed no discontinuities up to molar ratios of about 8. Apart from a deviation by the 10.1% nitrogen isotherm at small acetone activities, which may be due to experimental error, at any given activity there is a steady increase in the quantity of acetone adsorbed with increasing nitrogen content up to about 12%, and then a small decrease. The continuous nature of these results, which are in good quantitative agreement with those of the authors quoted above, is in accordance with the view that acetone is adsorbed by virtue of dipolar interaction or

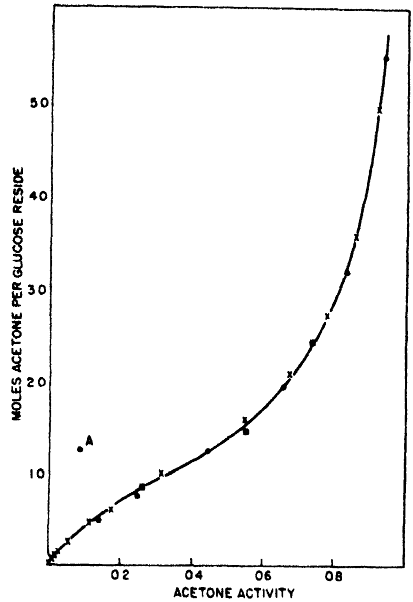

Fig. 1. Vapor phase isotherm at 20°C. for a cellulose nitrate of 12.2% nitrogen content. ● increasing adsorption (cellulose nitrate fiber); ■ decreasing adsorption (cellulose nitrate fiber); × increasing adsorption (reprecipitated cellulose nitrate).

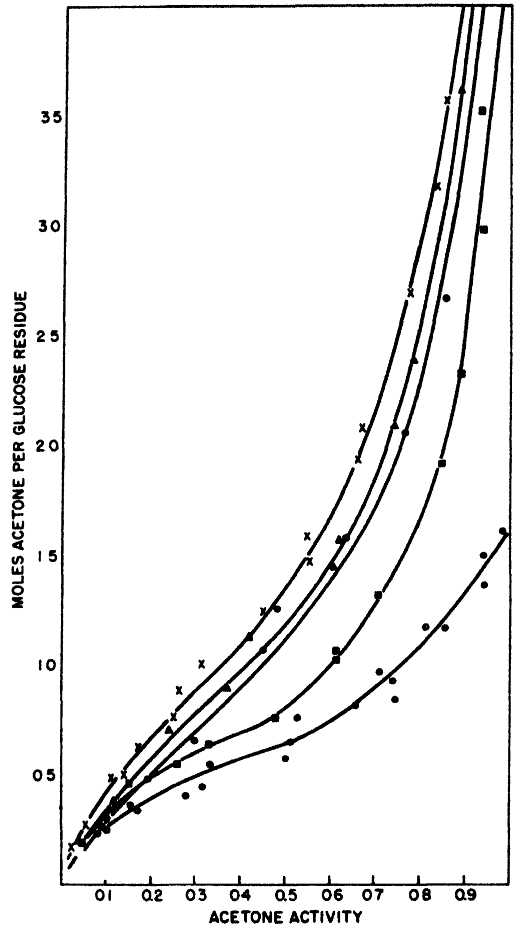

Fig. 2. Vapor phase isotherms at 20°C. for cellulose nitrates of different nitrogen contents. (⊙) 5.3%; (■) 10.1%; (▲) 11.2%; (×) 12.2%; (●) 13.7%.

other nonchemical bonding forces involving the presence of the nitrate groups. It appears that above 12% nitrogen content the nitrate groups interfere with each other so as to decrease slightly the strength of the forces responsible for adsorption.

ADSORPTION FROM THE LIQUID PHASE

The inert component of the liquid mixture from which acetone is to be adsorbed should have the following four main properties: (a) It should mix in all proportions with acetone. (b) It should give, when mixed with acetone, solutions obeying Raoult's law. (c) It should not be adsorbed, dissolve, or otherwise effect cellulose nitrate. (d) It should permit easy analysis.

It is doubtful if any liquid possesses all these properties. If the first requirement is not fulfilled, it follows that the partial vapor pressure of acetone, and hence its activity, is not a smooth continuous function of the composition of the mixture. It is clearly an advantage if the mixture is ideal so that such pressures may be calculated from

Raoult's law. The third condition is the most important, since at best it is a matter of considerable difficulty to work out the characteristics of the adsorption of a pure component from that of a mixture with another.

It was shown (McBain and co-workers (5)) that petroleum ether used by some other workers, is adsorbed only to a very small extent. Accordingly, the petroleum ether fraction boiling at 100-120°C., which at normal temperatures is miscible in all proportions with acetone, has been chosen as inert solvent. The existence of deviations from ideal behavior, however, is indicated by the separation of the mixture below about -25°C. into two distinct layers. These deviations are later considered in more detail. Although acetone is strongly adsorbed from such mixtures by cellulose nitrate, under the conditions used in this work there is no appreciable solution of the polymer in mixtures containing up to 40% by weight of acetone (i.e., up to activities of about 0.8).

Materials

A sample of good commerical petroleum ether (100-125°C.) was purified by shaking repeatedly with concentrated sulfuric acid, washing thoroughly, drying, and distilling. Comparison of the results obtained with this sample and with the original commerical material showed no differences and the commerical material was, therefore, used for most experiments. The acetone, containing not more than 0.5% of water, was not specially purified. Since vapor phase adsorption measurements (Fig. 2) prove that differences in the nitrogen content above about 11% did not seriously affect the isotherm, only one cellulose nitrate (12.2% nitrogen content), derived from a paper cellulose, was used. This cellulose nitrate, which was quite free from acid and had a very low ash content, was pumped out for several days in a vacuum desiccator and stored in stoppered bottles. Freshly dried cellulose nitrate did not behave differently from that which had been stored for several weeks after drying.

Experimental

A simplified form of the method of adsorption analysis (a modification of chromatography) described by Tiselius (13) has been used in studying the adsorption of acetone from mixtures with petroleum ether. Only adsorption cells in the form of cylindrical U-tubes have been used in the work described here, but the apparatus and the accuracy of the measurements could be considerably improved. In a convenient form of the apparatus, shown in Figure 3, a buret tube (A) and a length of glass tubing (B) of approximately the same internal diameter form the two arms of a U-tube and are joined at the base by narrower tubing. Just inside the latter below A is a sintered glass disk (D), upon which a weighed amount of the cellulose nitrate is packed firmly giving a plug (N) with a smooth horizontal upper surface. Before introducing the liquid mixtures from the tap funnel (F), the whole tube is evacuated on a good water pump through the tube (P) leading to both arms A and B, P and F being firmly supported by well fitting rubber bungs. In this way turbulence in the liquid column in A due to the dislodging of air bubbles in the plug (N) and air locking are avoided. When the tube has been well evacuated, the pump connection is closed by the screw clip (S) and sufficient liquid mixture is run into the tube from F to wet the whole of the cellulose nitrate plug. The screw clip may now be opened, putting both sides of the tube into communication with the atmosphere. The whole apparatus is placed in a thermostat and allowed to equilibrate for at least 15 minutes. Liquid mixture is then run very slowly into tube B from F, being controlled by a capillary leak (L) mounted on F, to give a head sufficient to force liquid through N at a rate of about 5 cc. per hour. The head in B necessary to give this flow rate depends upon the nature of the material, the density of packing, and length of the plug.

Under such conditions it is found experimentally (from refractive index measurements on liquid removed by a microsyringe) that the liquid first passing through N is pure petroleum ether, the acetone having been removed by adsorption on the cellulose nitrate (see Table I).

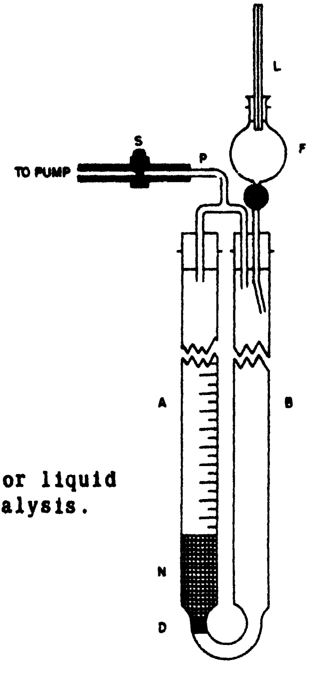

Fig. 3. Apparatus for liquid phase adsorption analysis.

When under the conditions of the experiment the cellulose nitrate becomes saturated with acetone, then unchanged liquid mixture passes through and a boundary, at which there is an abrupt change of refractive index, occurs between the pure petroleum ether and the unchanged mixture. The sharpness of this boundary determines the accuracy of measurement of the volume of liquid from which acetone has been removed. The composition of the original mixture being known, this retardation volume, as it has been termed by Tiselius (13), gives a measure of the total volume of acetone adsorbed by the weighed cellulose nitrate plug.

Observation of the position and character of the boundary between the petroleum ether and the mixture may be performed by any method utilizing changes in refractive index (Svedberg and Pedersen (14). In the present work, the diagonal schlieren optical method was used (Philpot (15), Svedberg and Pedersen (14), Alexander and Johnson

(16)). On a photograph of the limb A over the boundary region, the boundary appears as a peak (Fig. 4) consisting of a plot of the gradient (dn/dx) of refractive index (n) along the length (x) of the limb A. As in both the ultracentrifugal and electrophoretic methods the position of the boundary is taken at the x value corresponding to the maximum value of dn/dx. Error is introduced here if the peak is not sharp or is very asymmetrical. Since photographs of A show the horizontal buret graduations, a direct reading of the retradation volume can be made from them. Further, for a given optical setting (principally of the angle between the schlieren edge and the horizontal), the area of the peak is proportional to the total refractive index change at the boundary and this property can be utilized, as illustrated in Table II, to show the completeness of the adsorption from the liquid first emerging from the plug. To make quantitative use of this feature, however, it is necessary to make careful correction for irregularities in the base line of the peak.

TABLE I. Refractive Indices (±0.0002) of Pure Components, Original Mixture, and Liquid above Boundary

Composition of original mixture, cc. acetone/100 cc.	20	10
Refractive index of		
(1) Original petroleum ether*. . .	1.4082	1.4092
(2) Original acetone*.	1.3608	1.3579
(3) Original mixture	1.3972	1.4041
(4) Liquid above boundary.	1.4078	1.4087

*Differences in the refractive indices of petroleum ether and acetone are to be attributed partly to temperature differences and partly some variation in the punity of the liquids.

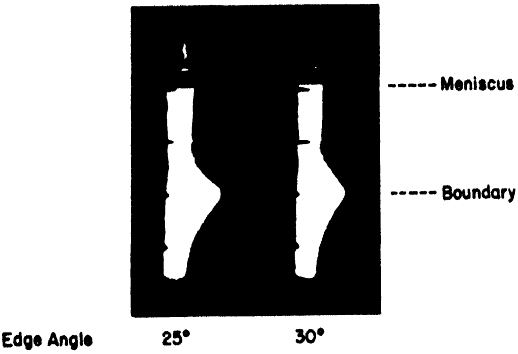

Fig. 4. Photographs of boundary caused by acetone adsorption from acetone-petroleum ether mixture (20 cc. acetone per 100 cc. mixture).

TABLE II. Schlieren Areas

Acetone concentration, cc./100 cc.	5	10	20
Corrected schlieren area. . .	0.29	0.58	0.92

DISCUSSION OF BOUNDARY FORMATION

At first sight it may appear strange that a sharp boundary between pure petroleum ether and unchanged mixture should appear rather than a steady increase in acetone concentration extending throughout the column of liquid which has passed through the plug. It should, however, be realized that the conditions for the formation of such a boundary are quite stringent and by no means realized with all systems. Of obvious importance are the following:

(1) Adsorption of the active component from the liquid mixture must occur rapidly.
(2) The rate of flow of liquid through the plug should be small and the plug tightly and evenly packed.
(3) The liquid above the boundary should be less dense than below.
(4) Observation of the boundary should not disturb it and should be made as soon as possible after its formation.
(5) Thermostatting is required to prevent large thermal disturbances, and freedom from mechanical shock is essential.

If these requirements are fulfilled, any small volume of liquid may be considered at any instant to be in equilibrium with the material of the plug with which it is in contact. Further, since owing to the close packed nature of the plug quite small volumes of liquid are associated with relatively large masses of cellulose nitrate, in the liquid passing through the plug the acetone concentration decreases rapidly with the length of plug traversed, reaching zero in quite short lengths.

It is convenient to consider three regions in the cellulose nitrate plug during flow (see Fig. 5). Region A is unaltered absorbent which initially, of course, extends throughout the plug. When the first small amount of liquid mixture enters the column, acetone is most rapidly adsorbed in the bottom layers, but corresponding with the decrease in acetone content as it flows upward the acetone uptake rapidly decreases with height. The region B, in which there is a rapid decrease of acetone adsorption with height, thus occurs at the bottom of the column as flow begins. With further flow the acetone uptake in the bottom layers increases gradually up to the equilibrium value corresponding to the acetone concentration of the original liquid mixture (region C) and although further flow cannot effect the acetone adsorption in these layers the extent of this region increases in height with flow (Fig. 5, II). Region B occurs above region C, however, but with the movement upward of the latter, region B is pushed ahead until finally region A (unchanged plug) has entirely disappeared (Fig. 5, III).

During the whole of this process acetone has been completely removed by the column and unchanged petroleum ether has emerged from the upper end. However, with the disappearance of region A, petroleum ether containing only a small quantity of acetone now emerges and the boundary begins to form in the liquid column. With further flow, region C migrates still higher, the concentration of acetone in any given layer in region B increases, the acetone concentration in the emerging liquid increasing correspondingly. Finally, as region B disappears, unchanged petroleum ether-acetone mixture emerges. Therefore, even if conditions 1 to 5 above are obeyed completely, a perfectly sharp boundary in the liquid column is not to be expected. It would appear theoretically* that two main factors (other than conditions 1 to 5) contribute to the sharpness of the boundary:

(6) The steepness of the slope of the adsorption isotherm.
(7) A large amount of solid in equilibrium with a given amount of liquid in any layer of the plug.

Only if the slope of the adsorption isotherm were infinite could be perfectly sharp boundary be obtained.

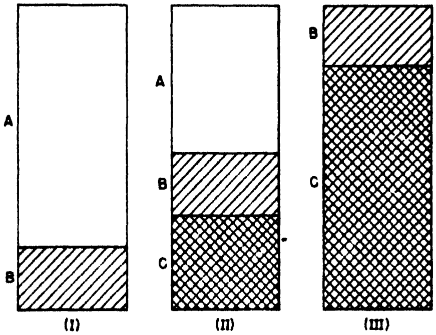

Fig. 5. Diagram illustrating the formation of the boundary in the liquid column.

To measure retardation volumes with accuracy, it is necessary that the boundary be sharp and it is advantageous if the curve of dc/dx (or dn/dx) v. x be symmetrical about the maximum value of dc/dx, where c is the concentration (and n the refractive index). It would be of great value in assessing the possibilities of the method if a systematic experimental study of the conditions required for the formation of a sharp boundary could be made. It has, for instance, been found that mixtures of petroleum ether and acetone flowing over cellulose acetate do not produce boundaries as sharp as over cellulose nitrate. This is most probably due to a flatter isotherm for acetone adsorption by cellulose acetate.

VERIFICATION OF EQUILIBRIUM NATURE OF ADSORPTION

It is essential to show that these adsorption analysis results really do refer to equilibrium states. If well pressed down, the cellulose nitrate plug and the liquid mixture flowing through it come into very intimate contact, so that liquid impoverished in acetone is continually replaced by unaltered mixture. It would, therefore, seem probable that equilibrium should be more rapidly attained by this method than by the more usual static techniques which rely on adsorbate replacement by diffusion.

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*See, however, Dole and Klotz (17), who for the sorption of gas from a flowing stream, state, without proof, that the adsorption wave should have a square wave front. Publication of the present paper was delayed by official regulations and it was complete before the work of Dole and Klotz became available.

As has already been stated, only slow rates of liquid flow were employed and, with varying length of plug and rates of flow (i.e., varying times of contact of liquid and solid), no systematic trends in the amount of acetone adsorption have been noted. Table III illustrates these points for two acetone mixtures with petroleum ether. Rates of flow here were made deliberately greater than those generally used. The following more direct test has also been used. To a weighed amount of cellulose nitrate in the vessel V connected to the mercury manometer M and the tap T (Fig. 6), a known volume of a mixture of acetone and inert low vapor pressure solvent (decalin) was added. The solid and liquid were thoroughly degassed by alternately evacuating with a Hyvac pump while frozen in liquid air and melting to release dissolved air. The vapor pressure (largely of acetone) at 20°C. was observed immediately after the final degassing,

TABLE III. Effect of Liquid Flow Rate and Length of Plug on Adsorption

Acetone concentration, cc./100 cc. of mixture	Weight of cellulose nitrate, g.	Retardation volume, cc.	Acetone adsorbed, cc./g.	Approx. rate of flow, cc./hour
20	1.06	2.54	0.60	-
	1.12	2.54	0.57	-
	1.30	3.25	0.63	-
	1.58	3.51	0.56	-
	1.89	4.80	0.64	14
	3.54	9.47	0.66	28
	4.78	11.2	0.59	27
10	0.622	3.1	0.50	9
	0.777	4.04	0.52	8
	1.115	5.02	0.45	-
	1.125	5.02	0.45	-
	1.339	6.21	0.47	19
	1.350	6.3	0.47	8
	1.401	6.62	0.48	13
	2.608	11.6	0.45	14

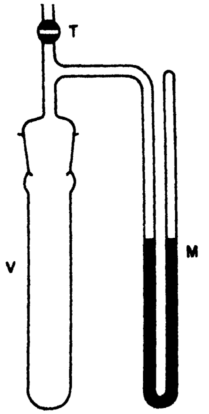

Fig. 6. Apparatus for the measurement of vapor pressure.

and no alternations in this value occurred with time. It was concluded therefore that by the time the first vapor pressure measurement was made (approximately one hour from first contact of cellulose nitrate and acetone solution), equilibrium had been established. Since this time is considerably shorter than that of an adsorption experiment and also in view of the observation that the degree of adsorption is independent of the length of plug and of the flow rate, the results obtained with the dynamic apparatus were accepted as referring to adsorption equilibrium.

Results

For each acetone concentration the volume of acetone adsorbed by 1 g. cellulose nitrate was determined, the mean of several observations under different conditions of flow rate and plug length being used to calculate the isotherm of Figure 7. The acetone concentrations varied from 2.5 to 20 cc. per 100 cc. of mixture with petroleum ether. At the lowest acetone concentrations, where the refractive index difference across the boundary was small and adsorption feeble, experimental accuracy was not great. Owing probably to the very small swelling of the cellulose nitrate plug under these conditions, smaller rates of flow than at higher acetone concentrations were found advantageous. Certainly at all other acetone concentrations (i.e., between 5 and 15 cc. per 100 cc.) except the highest, comparatively large flow rates were possible. At 20 cc. of acetone per 100 cc., the need for slower rates of flow was essential with the higher and looser acetone binding.

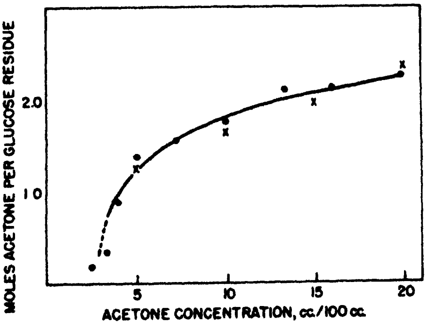

Fig. 7. The adsorption at 20°C. of acetone from mixtures with petroleum ether by cellulose nitrate of 12.2% nitrogen content. (●) Liquid phase results; (×) Vapor phase results from Figure 1.

In spite of these difficulties and an accurracy admittedly lower than in the vapor phase adsorption, the isotherm of Figure 7 is at least superficially very similar to those of Kargin and Papkov (2) and of Trogus, Tomonari, and Hess (1).

COMPARISON WITH VAPOR PHASE ADSORPTION

In order to compare liquid with vapor phase isotherms, it was necessary to determine the partial pressure of acetone as a function of concentration of the liquid mixture. Total vapor pressures of the mixtures were determined in the apparatus already described (Fig.

6). A suitable volume of each mixture was introduced into V and degassed as previously on a Hyvac pump until on freezing in liquid air no pressure was indicated on the manometer. The equilibrium vapor pressure at 20°C. for the mixture was then recorded. Figure 8 gives these total vapor pressures against volume concentrations of acetone. On the same diagram are shown the partial pressures of acetone calculated on the assumptions that (a) petroleum ether obeys Raoult's law; and (b) acetone obeys Raoult's law.

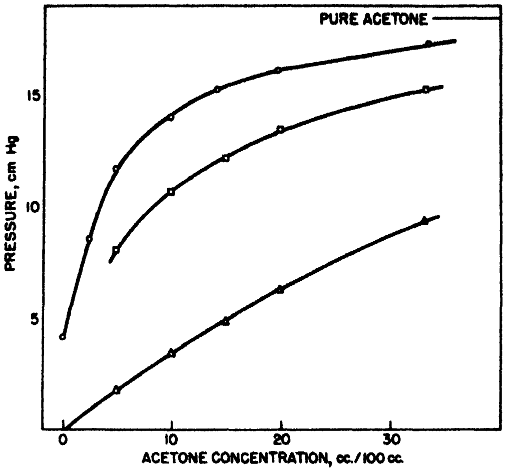

Fig. 8. Vapor pressure curves at 20°C. for mixtures of acetone and petroleum ether (b.p. 100-120°C.): (o) total pressure (experimental); (□) partial pressure of acetone calculated assuming petroleum ether obeys Raoult's law; (Δ) partial pressure of acetone assuming acetone obeys Raoult's law.

In view of the smallness of the vapor pressure of the petroleum ether and also the fact (Hildebrand (18)) that the almost pure component of a mixture generally obeys Raoult's law well, the first assumption may be safely accepted.

It is apparent from the total and acetone vapor pressure curves that large positive deviations from Raoult's law occur over the whole concentration range covered. The small expansion on mixing acetone and petroleum ether and the partial miscibility of these liquids below -25°C. is a further indication of the presence of such deviations. As a result, the rate of increase of the partial pressure of acetone with volume concentration is much smaller at higher than at lower concentrations. This leads to an apparent saturation vapor pressure of acetone at its higher concentrations, which is clearly responsible for the so-called limited acetone adsorption observed by Trogus, Tomonari, and Hess (1) and by Kargin and Papkov (2).

Thus, if the data for the vapor phase adsorption (Fig. 1) is plotted on Figure 7 by using the acetone partial pressure-concentration relation shown in Figure 8, the crosses shown in Figure 7 are obtained. When the nature of the experimental errors in the liquid phase adsorption are considered, as well as the approximations involved in deducing the acetone partial vapor pressure, the agreement with the liquid phase adsorption is surprisingly good and it is considered that within the limits of experimental error adsorption from the vapor phase and the liquid mixtures described are identical. The apparent limited adsorption of acetone by cellulose nitrate from mixtures of acetone and petroleum ether, which has been used by several authors as a basis of argument for the existence of compounds of acetone with cellulose nitrate, is thus spurious. The adsorption from such mixtures is essentially the same as that from the vapor phase, which, rather than possessing a limiting value, approaches infinity (for soluble cellulose nitrates) as the vapor pressure of pure acetone is reached. No indication of compound formation can therefore be deduced from this isotherm.

Further, it is clearly untenable to attempt to deduce the degree of solvation of cellulose nitrate dissolved in pure acetone by extrapolation procedures based on results from dilute swelling mixtures of acetone in petroleum ether or other inert solvent.

It should be mentioned here that though Petitpas (4), using different experimental methods, has not observed limits of adsorption for acetone-hexane mixtures, she claims that adsorptions from this mixture and from the vapor phase are somewhat different, the difference being attributed to the noninert character of hexane. This is, however, difficult to reconcile with the very low adsorption of hexane shown by McBain and co-workers (5).

Acknowledgment

We are grateful to Professor E. K. Rideal, F.R.S., for his encouragement and help during the course of this work, and to the Ministry of Supply for permission to publish it.

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Synopsis

The discrepancies in the published work on the interaction of acetone and cellulose nitrate are discussed and explained. Vapor phase adsorption isotherms for the adsorption of acetone by cellulose nitrate have been determined with an adsorption balance. They have been shown to be independent of the crystalline-amorphous ratio of the polymer but dependent upon its nitrogen content. In cellulose nitrates which are completely soluble in acetone, no limiting adsorption has been found. Adsorption analysis (a modification of chromatography) has been applied to the determination of the liquid phase adsorption by cellulose nitrate of acetone from mixtures with petroleum ether. In terms of the liquid mixture concentrations, there appears to be limited adsorption, but this is shown to be due to the nonideal nature of the solutions of acetone and petroleum ether. When allowance is made for this, the liquid and vapor phase isotherms are the same within experimental error and do not support the existence of compounds of acetone and cellulose nitrate.

Résumé

Les discordances, que présentent les publications concernant l'interaction de l'acétone et la nitrocellulose, sont soumises à discussion et interprétées. Les isothermes d'adsorption de la phase vapeur par adsorption de l'acétone par la nitrocellulose ont été déterminées à la balance d'adsorption. Ces isothermes d'adsorption sont indépendantes du rapport état cristallin/état amorphe du polymère, mais par contre, sont fonction de la teneur en azote. Les esters cellulosiques nitrés, entièrement solubles dans l'acétone, ne présentent pas de limites d'adsorption. L'analyse par adsorption (une modification de la chromatographie) a été appliquée à la détermination de l'adsorption de la phase liquide (acétonique) par la nitrocellulose au départ de mélanges avec l'ether de pétrole. En rapport avec les concentrations du mélange liquide, il semble y avoir une limite d'adsorption; cet effet, toutefois, est dû à la nature de l'état non-ideal des solutions acétone-éther de pétrole. Si on tient compte de cette correction, les isothermes d'adsorption de la phase liquide et vapeur sont les mêmes aux erreurs d'expériences près, et ne permettent pas de supposer l'existence de composés acétone-nitrocellulose.

Zusammenfassung

Die Verschiedenheiten in veröffentlichten Arbeiten über die Wirkung von Azeton auf Cellulosenitrat werden erörtert und erklärt. Mittels einer Adsorptionswage wurden Adsorptions-Isotherme der Azeton Adsorption durch Cellulosenitrat festgestellt. Sie waren unabhängig von den Verhaltniss krystallinischer und amorpher Masse, aber waren von den Stickstoffgehalt abhängig. In Cellulosenitrat das in Azeton gänzlich löslich ist wurde kein Grenzwert der Adsorption gefunden. Die Adsorptions-Analyse (eine Modifikation der Chromatographie) wurde augewandt zur Bestimmung der Adsorption in der flüssigen Phase von Azeton aus Mischungen mit Petroleumäther durch

Cellulosenitrat. Mit Bezug auf die Konzentration der Flüssigkeits-Gemische scheint eine Grenz-Adsorption zu bestehen, aber es wird gezeigt dass dies eine Folge der unidealen Eigenschaften von Azeton-Petroleumäther Mischungen ist. Wenn darauf Rücksicht genommen wird, sind die flüssigen und Gas-Phase Isotherme innerhalb experimentaller Irrtums gleich und unterstützen nicht die Existenz von Verbindungen zwischen Azeton und Cellulosenitrat.

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Copolymers of 1,3-Butadiene and 2,3-Dimethyl-1,3-butadiene*

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Polymers of 2,3-dimethyl-1,3-butadiene were prepared and used as rubber substitutes many years ago (1). In general they were more like plastics than like a rubber and for this reason were not continued in commercial competition with natural rubber. It seemed possible that substitution of 2,3-dimethyl-1,3-butadiene for styrene in GR-S type polymers might lead to products which would have interesting properties. This manuscript reports studies on the rates of copolymerization with butadiene, the extent of 1,2 and 1,4 addition of the moomers, and the intrinsic viscosity and solubility of the copolymers.

The 2,3-dimethyl-1,3-butadiene was furnished by the General Chemical Company and purified by distillation for most of these experiments. It was noted that 2,3-dimethyl-1,3-butadiene required very little modifier in the GR-S polymerization system (2), and hence it was necessary to decrease the amount of OEI used in the recipe in order to obtain polymers of fairly high molecular weight. This low modifier requirement was also noted in the 2-alkyl-1,3-butadiene series (3) of polymers; some examples are reported here (see Table III). Purification of 2,3-dimethyl-1,3-butadiene through the cyclic sulfone by the procedure previously reported by Craig (4) gave a sample of diene which polymerized faster and to a higher conversion than did the sample of distilled diene, but no important differences in the polymers were apparent.

Copolymers of 1,3-butadiene and 2,3-dimethyl-1,3- butadiene prepared in the mutual recipe were examined for the percentage of external and internal double bonds by perbenzoic acid titration.** It is of interest to note that 2,3-dimethyl-1,3-butadiene gives a polymer containing 15% of 1,2 units and 85% of 1,4 units, whereas butadiene gives the ratio 22 to 78%. The copolymers show values in between these extremes (see Table I).

Attempts to determine the composition of the polymer of 2,3- dimethyl-1,3-butadiene by C-methyl determinations according to the method of R. Kuhn and H. Roth as described by Pregl and Grant (5) gave only 56% of the calculated C-methyl value. No method, there-

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**We are indebted to Professor I. M. Kolthoff and Dr. T. S. Lee for these values and permission to include them in this manuscript.

fore, was available to determine accurately the composition of the copolymer, and the above calculations are based on the assumption that the copolymer composition is near that of the monomer composition of the polymerizing mixture.

TABLE I. Internal and External Double Bonds in 1,3-Butadiene - 2,3-Dimethyl-1,3-butadiene Copolymer

Butadiene, %	2,3-Dimethyl-1,3-butadiene, %	[η]	2,3-Dimethyl-1,3-butadiene: Internal double bonds	2,3-Dimethyl-1,3-butadiene: External double bonds	Butadiene: Internal double bonds	Butadiene: External double bonds
0	100	0.66	85	15	0	0
25	75	0.73	52	23	15	10
50	50	0.87	32	18	39	11
75	25	1.46	16	9	60	15
100	0	1.95	0	0	78	22

Time-conversion studies show that 2,3-dimethyl-1,3-butadiene requires a longer time to give 100% conversion than does 1,3-butadiene in the GR-S type system. Replacement of 25% of 1,3-butadiene by that amount of 2,3-dimethyl-1,3-butadiene slows down the polymerization to about the same extent as does complete replacement. Some variations in different runs are apparent, and this appears to be due to differences in the induction period.

EXPERIMENTAL

The 2,3-dimethyl-1,3-butadiene used boiled at 67.5-68°C.; n_D^{20} 1.4360. The material, purified through the cyclic sulfone, boiled at 67.5-68° and had n_D^{20} = 1.4390. The 1,3-butadiene used in these experiments was Phillips Petroleum Company research grade.

Polymerization of 2,3-Dimethyl-1,3-butadiene

In cases where 2,3-dimethyl-1,3-butadiene alone was polymerized the GR-S procedures (2) for charging, polymerizing, and working up of the polymer were used. The results are summarized in Tables II and III.

Copolymerization of 2,3-Dimethyl-1,3-butadiene with Butadiene

Charging. In cases where mixtures of monomers were used a special charging procedure was followed. The soap-water solution and potassium persulfate were placed in the polymerization bottles in the usual manner, after which the appropriate quantities of butadiene were added and the bottles securely capped. They were placed in a methanol both and slowly cooled to the vicinity of -30° by the addition of Dry Ice to the methanol. The bottles were then carefully opened one at a time and the appropriate weight of 2,3-dimethyl-1,3-butadiene which contained the required amount of mercaptan was added.

TABLE II. Polymerization of 2,3-Dimethyl-1,3-butadiene

Diene	Parts of diene	Parts of styrene	Parts of modifier per 100 parts of monomer	Time, hours	Conversion, %	Static solubility, %	Intrinsic viscosity, $[\eta]$
Butadiene	100	--	0.5 OEI	15	77.5	100	2.38
2,3-Dimethyl-butadiene	100	--	0.05 OEI	23.5	99.7	100	0.58
"	100	--	0.05 "	23.5	98.0	100	0.46
"	100	--	0	19	0	-	-
"	100	--	0	19	0	-	-
"	100	--	0.05 OEI	19	86.5	100	1.97[a]
"	100	-	0.01 "	18	68.5	100	2.58
"	100	--	0.01 "	18	68.0	100	2.38
"	100	--	0.01 cetyl mercaptan	18	67.0	100	2.86
"	100	--	0.01 " "	18	67.0	100	2.80
"	100	--	0.01 " "	20	77	100	2.84
"	100	--	0.01 " "	20	78	100	3.11
"	75	25	0.06 OEI	19	86.5	100	0.59

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[a] This sample of diene was purified through the cyclic sulfone.

These bottles after being recapped were placed in an ice-water bath while the remaining bottles were charged.

Polymerization. All of the bottles were allowed to stand at room temperature for one hour and were then placed in a pan of water; the temperature was slowly raised to 40° over the course of three-quarters of an hour, at which time the soap gels had softened. The bottles were shaken vigorously and placed in the 50° polymerization bath for the required polymerization time. The latices were coagulated with

TABLE III. Modifier Requirements in Polymerization of Substituted 1,3-Butadienes

Diene	Modifier (OEI) Parts per 100 diene	Time, hours	Conversion, %	Intrinsic viscosity, [η]
Butadiene	0.50	15	75	2.27
Isoprene[a]	0.30	15	75	1.15
2,3-Dimethyl-1,3-butadiene	0.05	19	56	0.60
2,3-Dimethyl-1,3-butadiene	0.01	18	68.5	2.40
2,3-Dimethyl-1,3-butadiene[a]	0.05	19	86.5	1.97
2-Ethyl-1,3-butadiene	0.10	24	87.5	1.16
2-n-Amyl-1,3-butadiene	0.10	40	64.0	1.40
2-Isopropyl-1,3-butadiene	0.20	26	72.5	1.62

[a] Indicates dienes purified through the cyclic sulfone.

TABLE IV. Copolymerization of 2,3-Dimethyl-1,3-butadiene with Butadiene

Butadiene, %	Time, hours	Conversion, %	Static solubility, %	Intrinsic viscosity, [η]
0	21	60	100	0.66
0	21	59	100	0.65
25	16	59	100	0.73
25	16	60	100	0.87
50	15	62	100	1.06
50	14	60	100	1.01
75	14	62	100	1.46
75	14	62	100	1.40
100	13	61	100	1.95
100	13	50	100	1.79

TABLE V. Copolymerization of Butadiene - 2,3-Dimethyl-1,3-butadiene.

Monomer charge					
Butadiene, g.	2,3-Dimethyl-1,3-butadiene, g.	Conversion, %	Time, hours	Static solubility, %	Intrinsic viscosity, [η]
20	-	28.0	5.18	100	0.88
		44.1	9.00	100	1.11
		66.7	13.00	100	1.44
		83.9	16.92	93	2.42
		96.0	22.00	78	1.41
		100	26.08	30	0.49
20	-	28.4	5.30	100	0.84
		43.5	9.26	100	1.07
		67.0	13.25	100	1.43
		83.9	17.17	94	2.36
		95.1	22.25	75	1.31
		99.4	26.33	34	0.46
15	5	33.7	5.50	100	0.84
		56.9	9.50	100	0.99
		74.0	13.42	100	1.39
		86.7	17.42	100	2.05
		94.5	22.58	100	1.45
		95.1	26.66	39	0.79
15	5	33.5	5.80	100	0.82
		75.5	13.67	100	1.40
		86.7	17.70	100	2.00
		93.9	22.75	100	1.60
		95.0	26.88	45	0.75

(Table V continued on next page)

TABLE V *(Continued)*

Monomer charge Butadiene, g.	2,3-Dimethyl-1,3 butadiene, g.	Conversion, %	Time, hours	Static solubility, %	Intrinsic viscosity, [η]
10	10	39.8	6.00	100	0.64
		57.3	10.00	100	0.76
		74.9	13.87	100	0.86
		86.1	17.92	100	1.19
		92.0	23.00	100	1.46
		94.5	27.17	89	1.39
10	10	40.3	6.25	100	0.78
		60.3	10.25	100	0.73
		76.1	14.08	100	0.78
		86.8	18.17	100	1.39
		93.1	27.38	91	1.44
5	15	34.6	6.5	100	—
		55.8	10.50	100	0.54
		72.2	14.35	100	0.57
		81.1	18.42	100	0.76
		87.0	23.30	100	0.66
		90.1	27.55	100	1.04
5	15	34.9	6.72	100	—
		57.0	10.75	100	0.45
		72.5	14.57	100	0.80
		81.3	18.75	100	0.69
		88.5	23.75	100	0.47
		90.3	27.72	100	0.57

brine-acid solution after the addition and dispersion of 5 ml. of a 3% phenyl-β-naphthylamine suspension. The polymers were washed with water and dried in an oven at 80° for twenty-four hours, during which time they were redivided several times to facilitate removal of the monomers and moisture. The results are summarized in Table IV.

Determination of C-Methyl Groups in Polymers of 2,3-Dimethyl-1,3-butadiene. The analyses of polymers of 2,3-dimethyl-1,3-butadiene for C-methyl groups was attempted since it was believed that their determination would serve as a method of evaluation of the number of 2,3-dimethyl-1,3-butadiene units in copolymers with butadiene. In order to test this method, samples of poly-2,3-dimethyl-1,3-butadiene were submitted for C-methyl determination by the method of Kuhn and Roth as described by Pregl and Grant (5).

Following are the results for a sample of poly-2,3-dimethyl-1,3-butadiene.*

Analysis: Calculated for CH_3, 35.90
Found for CH_3, 20.35

Time-Conversion Study of a Copolymerization of Butadiene and 2,3-Dimethyl-1,3-butadiene

The emulsion copolymerization of butadiene with 2,3-dimethyl-1,3-butadiene was carried out by using various ratios of butadiene and 2,3-dimethyl-1,3-butadiene in the mutual recipe.

Standard 4-oz. bottles were charged first with soap solution, then with potassium persulfate solution, and finally with butadiene. After an excess of butadiene was boiled off to remove air, the bottles were sealed with perforated caps using self-sealing GR-N gaskets; the appropriate quantity of 2,3-dimethyl-1,3-butadiene containing the required amount of mercaptan was injected through the cap by means of a hypodermic syringe. The bottles were allowed to stand at room temperature for twenty minutes and then placed in a 50° polymerization bath. Sampling was carried out as described by Frank, Adams, Blegen, Deanin, and Smith (6). The results of the polymerization are shown in Table V.

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*Analysis by Clark Microanalytical Laboratories, Urbana, Illinois.

Synopsis

Some experiments on the polymerization of 2,3-dimethyl-1,3-butadiene and its copolymerization with butadiene are reported. This monomer requires very little modifier as compared to butadiene.

Résumé

Certaines expériences de polymérisation du 2,3-diméthyl-1,3-butadiène, et de copolymérisation de celui-ci avec le butadiène ont été effectuées. Ce monomère ne nécessite l'emploi que de faibles quantités de modificateur, par comparaison avec le butadiène.

Zusammenfassung

Es werden eine Reihe von Untersuchungen der Polymerisation von 2,3-Dimethyl-1,3-butadien und seiner Mischpolymerisation mit Butadien berichtet. Dieses Monomer benötigt viel weniger Umwandler als Butadien.

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Polymerization in a System of Discrete Particles

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INTRODUCTION

The process of polymerization is generally regarded as a chain reaction which involves at least three distinct steps: initiation, propagation, and termination of reaction chains. Although a number of different reactions have been suggested to account for the process of initiation, there seems to be general agreement about the character of the propagation and termination reactions. The former is generally assumed to involve a simple collision between the monomer and an active polymer chain, while the termination reaction is considered to be a bimolecular process involving the collision of two active centers. The most important evidence for the conception of a bimolecular termination reaction is the widespread observation that when the polymerization reaction is initiated in a bulk system by the action of light or by catalysts, the rate of the over-all reaction is proportional to the square root of the light intensity or catalyst concentration (1-4). Now, since this step is a controlling factor in the rate of polymerization, it follows that any condition restricting the termination reaction will increase both the rate of polymerization and the chain length of the polymer. Further, it appears that diffusion must be considered as a possible factor limiting chain termination, since the energy of activation for this step is low and because large molecules are involved (5). In any case, the conception of a diffusion controlled reaction has been put forward by Norrish and Smith (6) to account for the results of certain polymerization experiments where it was found that methyl methacrylate polymerized more quickly in a solvent which caused the polymer to be precipitated than in a good solvent for both polymer and monomer. Similar experiments have been reported by Haward (7) using methyl isopropenyl ketone. In each case, the increased rate of polymerization was accompanied by an increase in the intrinsic (or inherent) viscosity of the polymer formed. In other experiments by Melville (8), a more refined technique was used, and it was specifically shown that when vinyl acetate was polymerized in a nonsolvent for the polymer, the velocity constant for the chain termination reaction was reduced.

Once the conception of a diffusion-controlled reaction is accepted, it would also seem reasonable to anticipate that polymerization will be affected by the viscosity of the medium in which the reaction occurs, in view of the very large changes in viscosity which occur in a monomer polymerizing in bulk. Therefore, it is relevant to note that Trommsdorf (9), using methyl methacrylate, has obtained very considerable experimental support for the existence of this effect. For example, he showed that if the viscosity of methyl methacrylate monomer is increased by dissolving cellulose propionate in it, the velocity of polymerization can be increased.

However, it appears that all monomeric materials do not behave similarly in respect to the degree of the viscosity effects observed. For instance, it has been shown by Haward (8) in a review of published work that styrene is much less susceptible to diffusion effects in polymerization than some other monomers–and especially methyl methacrylate. Obviously, the existence of well established viscosity and precipitation effects in polymerization further supports the idea of a bimolecular termination reaction.

There is, however, one consequence of the conception of a bimolecular termination reaction in polymerization which has not yet been the subject of theoretical investigation. Clearly, a polymerization system dependent on a bimolecular termination process cannot be indefinitely subdivided without causing drastic alternations in the mode and character of the reactions. For example, if a bulk polymerization could be suddenly divided up so that each compartment contained only one active center, it would be expected to continue the process of chain propagation, (i.e., polymerization) indefinitely without any further initiation process. At first this may seem to be a remote proposition of little practical interest, but it must be remembered that the active centers in a polymerizing medium are themselves present in very small concentration, so that there is no reason to assume that the characteristic particle containing only one of them will be unduly small. In any case, wherever the system is subdivided into drops which contain only a small number of active centers, it will be necessary to make some amendment to allow for the fact, since the assumption based on the existence of large assemblies of reacting molecules customarily involved in chemical kinetics will no longer apply.

In this paper it is proposed to discuss the problem of compartmentalization as applied to a simple polymerizing system. The discussion proceeds in three distinct stages. First, some typical systems polymerizing in bulk are considered and the number of active centers at any given time is calculated using the absolute values of the propagation constant which have recently become available. This makes it possible to estimate the volume of monomer associated with one active center and the diameter of the "critical drop" and also to estimate the rate of polymerization of drops of different sizes containing one active center. Second, the question of discrete systems is considered in relation to a particular standard polymerization reaction and the results demonstrated for simple models using two different initiation reactions. Finally, the character of the assumptions made and the conclusions reached is discussed in relation to the processes of dispersion polymerization.

ESTIMATION OF THE SIZE OF A DROPLET CONTAINING A SINGLE ACTIVE CENTER

In this and subsequent discussions, we shall mainly consider systems consisting of a pure monomer which has been polymerizing just long enough to give an equilibrium between initiation, propagation, and termination reactions. For the purpose of calculating the size of the critical droplet, it is then necessary to know the constant of the propagation reaction (k_p), the over-all rate of polymerization (R), and the concentration of monomer (M), which in this case is that of the pure material. Now the constants of the propagation reaction have recently been measured by Burnett and Melville (10) and by Bartlett and Swain (11) for vinyl acetate* and by Bamford and Dewar (12,13) for styrene and methyl methacrylate. With regard to the rate of reaction, it is clear that once the constant of the propagation reaction has been measured the number of active centers will depend directly upon it and can be calculated for any rate of polymerization using the formula given below. Thus the diameter of the critical drop, which in this calculation is simply the total volume divided by the number of active centers, will depend on the cube root of the assumed rate of polymerization. In Table I, R has been arbitrarily chosen as that rate of reaction which would give complete polymerization in 10 hours (36,000 seconds). However, a variation in this rate by a factor of 10 will only alter the calculated drop size by a factor of 2.2, and for this reason the sizes given in Table I will correspond with the conditions in a wide range of practical polymerization reactions. The diameter (d, cm.) of the critical drop containing only one active center is derived as follows:

TABLE I. Size of a Critical Droplet Containing only One Active Chain for Systems Polymerizing at a Standard Rate

	Temperature	k_p, mole/liter seconds	d, cm.
Vinyl acetate	15.9° C.	586 (10)	3.9×10^{-5}
	25° C.	1100 (11)	4.8×10^{-5}
Styrene	25° C.	18.7 (12)	1.3×10^{-5}
Methyl methacrylate	25° C.	150 (13)	2.5×10^{-5}

$$\text{Volume of a single drop (liter)} = \frac{d^3\pi}{6000} = v$$

$$\text{Number of drops per liter of monomer } N = 1/v$$

Hence with one active center per drop there are N/N_0 moles of active centers per liter where N_0 is the Avogadro number. Therefore:

and:

$$\text{Rate of polymerization} = \frac{Nk_p(M)}{N_0} = R$$

$$R = \frac{6000}{\pi d^3 N_0} k_p(M)$$

hence:

$$d = {\frac{6000\ k_p(M)}{\pi R N_0}}^{1/3}$$

---

*Some differences between these workers need not concern us here, as the figures they obtain for the propagation reaction agree very well. The differences in their results affect the other constants.

Examination of these figures shows that the droplets are of colloidal dimensions, i.e., large compared with the size of a monomer molecule. Further, it is probable that for most purposes, the figures for the calculated diameters are on the low side, since most polymerizations are carried out at temperatures considerably above the ones used in the experiments in which k_p was measured, and the values of k_p are, therefore, likely to be low. Taking a value of 6500 cal. as the activation energy of the propagation reaction (12), it can be shown that the use of temperatures 50°C. above those given here would lead to an increase in the diameter of the critical drop by a factor of 1.7. Therefore, it seems reasonable to conclude that the size of the critical drop will generally lie between 10^{-5} and 10^{-4} cm. (0.1-1 micron) whenever the rate of polymerization does not depart from the one assumed by more than an order of magnitude. Such drop sizes, although of colloidal dimensions, will greatly exceed the weight of the individual polymer molecules. For instance, a single tightly-coiled polymer molecule having diameter of 10^{-5} cm. and a density of unity would have a molecular weight of about 3×10^8, i.e., about a thousand times that of a polymer having a molecular weight of 300,000. Thus the first of the questions raised in the introduction is answered. It is concluded that the existence of particles containing only small numbers of reacting molecules is a possibility in any system in which the monomer is dispersed on a colloidal scale and the consequent problem of how such systems behave is, therefore, of practical as well as theoretical interest.

RATE OF POLYMERIZATION OF A DROP HAVING A SINGLE ACTIVE CENTER

In the previous section, the volume of liquid associated with one active center has been calculated for a given rate of polymerization and expressed in terms of the diameter of a spherical drop. It is equally possible to consider the case of a drop having a single active center and to consider its rate of polymerization. Assuming that the monomer disappears according to a first-order kinetic, neglecting collisions with the surface of the drop, the following relation can be obtained:

$$\frac{d(M)}{dt} = -\frac{k_p(M)}{N_0 v}$$

where v is the volume of the drop ($\pi d^3/6000$ liters). It follows that the half-time of polymerization ($t_{1/2}$) of the drop will be given by:

$$t_{1/2} = \frac{N_0 \pi \ln_e 2}{6000 k_p} d^3$$

Thus according to this method of estimation, time for the polymerization of such a drop depends on the cube of its diameter. This suggests that where very small drops are formed in a polymerizing system, they are liable to be completely polymerized in a short time. Values of the half-life at 25°C. given by this relation are plotted in Figure 1; as a further consequence it follows that where a small polymerizing drops are dispersed in a common medium the smallest drops are likely to contain a lower concentration of monomer than the larger ones.

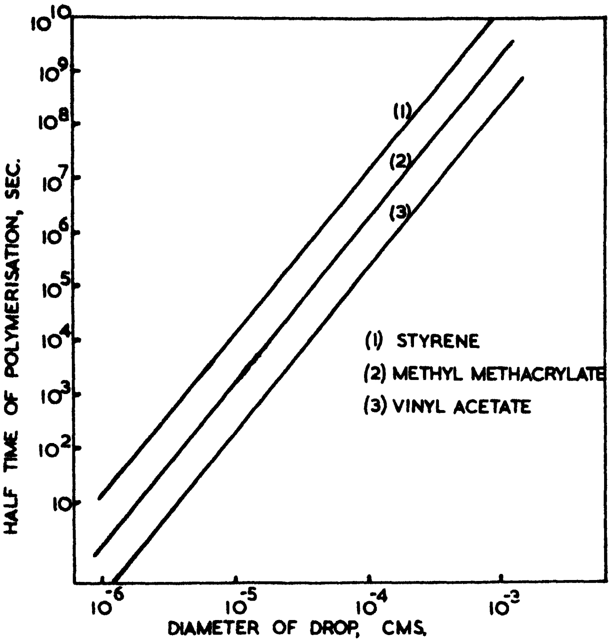

Fig. 1. Half-time of polymerization of drops containing a single active center.

PROBLEM OF POLYMERIZATION IN COMPARTMENTALIZED SYSTEMS

1. Behavior of the Standard Bulk System

All the polymerizations considered in this section are derived from a single model of a standard bulk system consisting essentially of pure monomer. It is assumed that k_i' moles $\sec^{-1}$ liter^{-1} reaction chains are initiated by the action of light, heat, or a catalyst and that the termination and propagation constants are k_t and k_p in the same units. Later it will be assumed that these constants are not affected when the system is divided into small compartments. In actual fact, this assumption will only be an approximate one, since the constants will be slightly affected by the further restriction in the number of arrangements in a single system. Thus the reaction is represented schematically as follows:

$$\begin{array}{ll}
X \longrightarrow \overset{x}{M}_{\text{active}} & k_i' \\
\overset{x}{M} + M \longrightarrow \overset{x}{P}_2 & k_p \\
\overset{x}{P}_n + M \longrightarrow \overset{x}{P}_{n+1} & k_p \\
\overset{x}{P}_n + P_m^x \longrightarrow P_{n+m} & k_t
\end{array}$$

In connection with the proposed initiation mechanism, it should be recognized that in many cases it will be equivalent to terms containing the monomer concentration, although this is not included in the proposed treatment. For instance, if c is the catalyst concentration the rate of chain initiation is often equated to $k_i cM$ (14) which would, therefore, be equivalent to the quantity k_i' used here. It is considered desirable to use an initiation of this form here because it allows a more generalized approach and because the intention is to investigate the effect of subdivision on the system and not to deal with the results of changes of concentration. As regards the termination reaction, the radicals are assumed to recombine, but disproportionation is also possible and this would cause the values for the average degree of polymerization for the bulk system to be halved; other molecular weight expressions given later would also be affected, but not so as to alter the general nature of the conclusions reached. With these constants the following relations may be deduced for the bulk system.

$$\text{Rate of polymerization} = R = k_p(M)\left(\frac{k_i'}{k_t}\right)^{1/2}$$

$$\text{Average degree of polymerization} = \frac{2k_p(M)}{(k_i'k_t)^{1/2}}$$

$$\text{Number of active centers} = N_0\left(\frac{k_i'}{k_t}\right)^{1/2} = \frac{RN_0}{k_p(M)}$$

This system is then assumed to be divided up into discrete particles, so that one liter gives N equal drops of volume v liters where $N = 1/v$. With regard to the initiation reaction, it soon becomes clear that it makes a good deal of difference whether the active centers are generated singly or in pairs, and two types of initiation are, therefore, considered. Other steps in the polymerization process, such as branching or chain transfer, are not examined, although it is felt that the latter would not be likely to invalidate any of the conclusions reached, except in regard to the molecular weight of the product, provided that it took place wholly within the drop. However, if chain transfer, a termination, takes place at the surface of a drop, this would profoundly affect the conclusions reached. It should also be noted that wherever these results are to be considered in relation to catalyzed reactions, and where chain initiation is assumed to occur within the drops, it must also be assumed that the catalyst is present in a quantity sufficiently large for statistical fluctuations in its concentration to be neglected.

2. Bimolecular Reactions with Small Numbers of Molecules.

Consideration of the arrangement of molecules in a theoretical lattice with s sites on a coordination number Z leads to the following relation for the number of molecules with immediate neighbors:

$$\text{Number of pairs} = \frac{Z}{2s}N(N-1)$$

provided $s >> N$.

This relation corresponds to the terms c^2v in the usual equation for a bimolecular reaction. Further, since $c = N/N_0v$, it follows that the correct concentration term for a bimolecular reaction is $N(N-1)/N_0^2v$, which should be applied wherever the number of reacting molecules may be small. This quantity becomes the same as that derived from c when N is large, and when $N = 1$ it becomes zero, which is, of course, correct for a single molecule. This relation takes no account of collisions with the surface of the drop in small drops.

2. Polymerization in Drops with Initiation by Formation of Single Active Centers

When the behavior of the standard chain reaction is considered in relation to small discrete systems it soon becomes clear that the results depend on the manner in which the chains are initiated and particularly on whether they are started singly or two at a time. In this section, the case where chains are started one at a time is considered. For this discussion it does not matter whether the chains are started inside the drops or whether they reach the drops by diffusion from an external continuous phase. In each case it is assumed that the rate at which centers reach a drop is proportional to the volume of the drop. This assumption is clearly reasonable in the case of internal generation of active centers, but in the case of external generation this would only apply when there was a steady generation of growing chains in a fixed volume of a continuous phase, so that the average rate at which they reached the single drops would be inversely proportional to the number of drops and hence directly proportional to their volume. In other cases this rate might be expected to be proportional to the area of a drop. However, it is not to be expected that this difference will seriously affect the results, as it will be seen that they are mainly of a qualitative nature.

In this and subsequent treatments it is always assumed that all the drops are of the same volume, v, and consideration is given to changes in the number of drops, n_p, having p active centers. Thus, the standard drop may gain one active center to give a drop with p + 1 active centers or by a process of mutual chain termination it may lose two active centers and yield a drop with p - 2 active centers.

Thus n_p will depend on the equilibrium between the following processes:

$$n_{p-1} \longrightarrow n_p \longrightarrow n_{p+1} \qquad \text{Initiation}$$

$$n_{p+2} \longrightarrow n_p \longrightarrow n_{p-2} \qquad \text{Termination}$$

The rate at which drops go from (p - 1) → p active centers is:

$$k_i' N_0 v n_{p-1}$$

and the rate at which drops go from p → (p + 1) is similarly:

$$k_i' N_0 v n_p$$

On the other hand, from the termination reaction, it follows that the rate of generation of drops with p active centers from those with (p + 2) active centers is:

$$1/2 \; k_t n_{p+2} \frac{(p+1)(p+2)}{N_0 v}$$

the factor 1/2 being introduced by the fact that each step involves the destruction of two active centers. Similarly the number changing from p → (p - 2) is given below by:

$$1/2 \; k_t n_p \frac{p(p-1)}{N_0 v}$$

Now assuming a steady state with regard to drops having p active centers:

$$k_i' N_0 v n_{p-1} + 1/2 \; (k_t/N_0 v) \; n_{p+2} \; (p+1)(p+2) =$$

$$k_i' N_0 v n_p + 1/2 \; (k_t/N_0 v) \; n_p (p-1) p$$

These relations do not lend themselves to exact treatment. Nevertheless, we can write without approximation:

$$n_2 = \frac{k_1'}{k_t} N_0^2 v^2 n_0 \tag{1}$$

$$n_3 = \frac{1}{3}\frac{k_1'}{k_t} v^2 N_0^2 (n_1 - n_0) \tag{2}$$

$$n_4 = \frac{1}{6}\frac{k_1'}{k_t} N_0^2 v^2 \left\{\frac{k_1'}{k_t} v^2 N_0^2 n_0 - (n_1 - n_0)\right\} \tag{3}$$

from which it follows that $n_2, n_3, n_4 \longrightarrow 0$ as $v^2 \longrightarrow 0$, and the same can be shown for higher values of p. This is clearly a reasonable result. For as the drop becomes smaller, the lifetime of two or more active centers within it becomes short, i.e., the number of the drops with two or more active centers tends to zero.

Also, since neither n_3 nor any of the other quantities in these relations can be negative, it follows from equation 2 that $n_1 > n_0$, and from equation 3 that:

$$(n_1 - n_0) < \frac{k_1' v^2 N_0^2 n_0}{k_t}$$

consequently it is concluded that $n_1 \longrightarrow n_0$ as $v^2 \longrightarrow 0$, and since higher values are now absent as $v^2 \longrightarrow 0$:

$$n_1 \longrightarrow N/2 = 1/2v^*$$

Under these conditions, n_1 is equal to the number of active centers in the system and the rate of polymerization is therefore given by the relation:

$$R = \frac{k_p(M)}{2vN_0} = \frac{Nk_p(M)}{2N_0}$$

i.e., as the drop size is diminished the rate of polymerization becomes proportional to the number of drops and independent of the rate of initiation, that is to say, independent of catalyst concentration or light intensity.

Similarly the degree of polymerization becomes:

$$\frac{Nk_p(M)}{k_1' N_0}$$

These two relations will, of course, only apply when the rate of reaction calculated in this manner is considerably greater than that of the bulk system, that is:

$$\frac{Nk_p(M)}{2N_0} >> k_p(M)\left(\frac{k_1'}{k_t}\right)^{1/2}$$

---

*This relation can also be deduced by the following argument. When the drop size is small the lifetime of a drop containing two active centers will be small. Hence, the history of any drop will consist of changing from zero to one active center and then to zero again. The time spent in each state will be the reciprocal of the probability of gaining a new active center, and so, on an average, half the drops will contain one active chain at any given time.

or when:

$$\frac{N}{2} \gg \frac{R_{bulk} N_0}{k_p(M)}$$

which goes back to our original calculation and shows that the number of drops must in fact be much more than twice as great as the number of active centers in the corresponding bulk system.

4. Polymerization in Drops with Initiation by the Simultaneous Formation of Two Active Centers

This type of initiation could occur either by the action of U.V. light (11) or by the decomposition of a catalyst such as benzoyl peroxide (15,16), e.g.,

$$(C_6H_5COO)_2 \longrightarrow C_6H_5^{x} + CO_2 + C_6H_5COO^{x}$$

Obviously, if initiation takes place by such a process within isolated drops, and if the termination process is that of the mutual termination of two reactive chains, then all the drops in such a system will contain an even number of active centers, and a drop will always gain or lose two active centers at a time. In treating such a system, it is convenient to consider the gain or loss sustained in unit time by the n_p drops which have p active centers in them, i.e., the equilibria:

$$n_{p+2} \rightleftharpoons n_p \rightleftharpoons n_{p-2}$$

Then the number of drops going from p to (p + 2) is given by the relation:

$$1/2\ k_i' N_0 v n_p$$

and the number going from p to (p - 2) is:

$$\frac{1}{2}\,\frac{k_t (p)(p-1) n_p}{N_0 v}$$

Together these represent the total reduction in the number of drops having p active centers. In the same time, the gain in the number of drops having p active centers is:

$$1/2\ k_i' v n_{p-2} N_0 + \frac{1}{2}\,\frac{k_t (p+1)(p+2) n_{p+2}}{N_0 v}$$

and since in the steady state these are equal, the general distribution of active centers within the drops will be given by the relation:

$$N_0^2 v^2 k_i' n_{p-2} + k_t n_{p+2} \cdot (p+1)(p+2) = n_p [N_0^2 v^2 k_i' + k_t \cdot p(p-1)]$$

From this, it can be shown that if n_0 is the number of drops with zero active centers, then the number with two, four, six, and p active centers is given by the terms of the expansion:

$$n_0 \left[1 + \left(\frac{k_i'}{k_t} v^2 N_0^2 \right) \frac{1}{\lfloor\underline{2}} + \left(\frac{k_i'}{k_t} v^2 N_0^2 \right)^2 \frac{1}{\lfloor\underline{4}} \ldots + \left(\frac{k_i'}{k_t} v^2 N_0^2 \right)^{p/2} \frac{1}{\lfloor\underline{p}} \right] \quad (4)$$

i.e., to the terms of the expansion of:

$$n_0 \cosh \left(\frac{k_i'}{k_t} v^2 N_0^2 \right)^{1/2} \quad (5)$$

where this quantity is itself equal to the total number of drops, i.e., to 1/v.

To find the total number of active centers, simply multiply each term in equation 4 by the number of centers in the drop (p), so that it now becomes:

$$n_0\left[\frac{k_i'}{k_t}v^2N_0^2+\left(\frac{k_i'}{k_t}v^2N_0^2\right)^2\frac{1}{\underline{|3}}\cdots+\left(\frac{k_i'}{k_t}v^2N_0^2\right)^{p/2}\frac{1}{\underline{|p-1}}\right]=$$

$$n_0\left(\frac{k_i'}{k_t}v^2N_0^2\right)^{1/2}\sinh\left(\frac{k_i'}{k_t}v^2N_0^2\right)^{1/2}$$

and therefore substituting for n_0 according to equation 5 the rate of reaction becomes:

$$= n_0 k_p(M)\left(\frac{k_i'}{k_t}v^2N_0^2\right)^{1/2}\sinh\left(\frac{k_i'}{k_t}v^2N_0^2\right)^{1/2}$$

$$= k_p(M)\left(\frac{k_i'}{k_t}\right)^{1/2}\tanh\left(\frac{k_i'}{k_t}v^2N_0^2\right)^{1/2}\ \text{moles liter}^{-1}\,\text{sec}^{-1}$$

and in this expression, the last term tends to zero as v→o, i.e., as the number of drops is increased, the reaction is suppressed. This can be seen qualitatively by noting that as the drop size is diminished the lifetime of two newly formed active centers in it is also reduced. Under these circumstances, they can never escape from each other and recombine before an appreciable amount of polymerization has taken place. The rate of polymerization of such a system is, therefore, always less than that of the pure monomer, and stops at a high degree of subdivision. The chain length (degree of polymerization) is also reduced to a similar extent, i.e.:

$$\text{Degree of polymerization} = \frac{2k_p(M)}{(k_i'\cdot k_t)^{1/2}}\tanh\left(\frac{k_i'v^2N_0^2}{k_t}\right)^{1/2}$$

Finally, it may be noted that when very small drops are considered, the values of k_p assumed for the bulk reaction may not hold exactly since the behaviour of single catalyst fragments will not be the same as that of a long chain.

5. Incompletely Isolated Drops

So far, it has been assumed that each drop is completely isolated from its neighbors, so that no contact between any two drops is possible. However, under certain conditions, it is possible to treat a system without making this assumption. For this purpose, we assume instead that a number of the drops coalesce and then separate in unit time. This is undoubtedly a rather artificial type of mechanism, though in the treatment given it is not also necessary to assume that the drops are all of equal size, but it does make it possible to specify the system and so enables a simple treatment to be applied. However, it is assumed that the number of drops is large, so that the lifetime of two or more active centers in a drop is small and as a result of coalescence only a relatively small proportion of the drops have an active center at all. The case of generating active centers one at a time is the only one investigated, since in a nonisolated system the occurrence of drops with an odd number of active centers is to be expected in any case.

Let x be the total number of active centers in the system. Then the rate of formation of centers within the drops is:

$$k_i'\left(1-\frac{2x}{N}\right). \text{ Also the rate of destruction } = q\frac{x^2}{N^2}$$

therefore in the steady state:

$$x = k_i'\frac{N}{q}\left[\left(1+\frac{q}{k_i'}\right)^{1/2} - 1\right]$$

it follows that if q/k_i' is small, i.e., the drops are nearly isolated, $x = N/2$ as before. But if q/k_i' is large, which is the case under consideration, then x approximates to $N(k_i'/q)^{1/2}$ and the rate of polymerization becomes:

$$\frac{k_p(M)N}{N_0}\left(\frac{k_i'}{q}\right)^{1/2}$$

i.e., proportional to N and to the square root of the rate of initiation over coalescence.

The chain length will be:

$$\frac{2k_p(M)N}{N_0\,(k_i'q)^{1/2}}$$

In consequence, the condition for an increased rate of reaction and chain length will be:

$$\frac{N}{q^{1/2}} > \frac{N_0}{(k_t)^{1/2}}$$

and the relations will, in fact, only hold when the left-hand side of this inequality is much the larger.

DISCUSSION

Three main conclusions follow from the proceeding treatment of the problem of polymerization in isolated systems.

(a) Whenever a monomer like methyl methacrylate, vinyl acetate, or styrene polymerizes in a dispersed system containing droplets having a diameter below 10^{-4} cm., special consideration must be given to the effect of compartmentalization on the termination reaction. (b) Where active polymer chains are generated singly within a system of small drops, the rate of polymerization and chain length will increase as the size of the drops is diminished. With decreasing drop size, the rate of reaction should become proportional to the number of drops into which the system is divided. This conclusion also applies if some limited form of contact between the drops is allowed. (c) If active polymer chains are formed in pairs in completely isolated drops, the rate of reaction and chain length are reduced as the drop size is diminished.

In view of these conclusions, it is of interest to consider briefly the question of their application to the forms of dispersion polymerization used at the present time. These may be divided into two types.

True emulsion polymerization, where an emulsifying agent and a catalyst soluble in the water phase are used, and bead or pearl polymerizations, where a catalyst soluble in the monomer is employed, together with various types of dispersing agent. Clearly, the condition of the generation of active chains one at a time is likely to be fulfilled in any system where free radicals are generated in the continuous aqueous phase. It has further been clearly established by Siggia, Hohenstein, and Mark (17) and by Harkins (18) that drops below 10^{-4} cm. occur in polymerizing emulsions in the case of styrene. Similarly, particle sizes ranging from 2×10^{-5} cm. to 4×10^{-6} cm. have been reported by earlier workers in the case of synthetic rubber latex (19,20). Indeed, Harkins (18) emphasizes the role of very small monomer polymer particles in emulsion polymerization and specifically mentions the possibility that particles containing only one active center are formed during the polymerization process. According to Harkins, it would be possible to connect the occurrence of a combination of high molecular weight and a fast reaction rate in emulsified systems with the existence of finely dispersed drops or particles. This conclusion would also be in accordance with the observations of Siggia, Hohenstein, and Mark (17) and of Harkins (18) that increasing the concentration of emulsifying agent leads to smaller drops and a faster reaction rate. However, since the emulsifier concentration is varied, other explanations of this effect may also be possible. Nevertheless, the observed effect is an increase in the rate of polymerization as the number of drops increases, and this conforms with the predictions given above.

In two recent papers, it has been shown by Baxendale, Evans, and Kilham (21,22) that a restriction of the termination reaction with methyl methacrylate did exist in an emulsified system. This could be an effect of subdivision. However, the same behavior can also be explained by the conception of polymerization occurring in viscous aggregates, where the termination reaction is controlled by diffusion. Such effects are known to be large in the case of methyl methacrylate. Thus, diffusion control can operate in the same way as the compartmentalization effect in emulsion polymerization, and it is not easy to distinguish between the two processes. However, this might be done by working with a solution of a monomer in a good solvent for the polymer dispersed together in water. In this case, the formation of viscous aggregates of high viscosity would be unlikely.

With regard to the third conclusion, considerable doubt must be expressed with regard to the direct applicability of the model in which radicals are formed in pairs. The reason for this is that even minor departures from the assumptions of the model will lead to the accumulation of drops having odd numbers of active centers in the system and to a consequent increase in reaction rate as the drop size is reduced. If any real systems do correspond with the behavior of this model, they would obviously be those in which a catalyst soluble in the monomer but insoluble in water is used. Nevertheless, it would appear that a number of factors will prevent these systems from corresponding exactly to the model chosen in this paper. These include:

(a) the pre-existence of some free radicals in the mixture before it is dispersed;

(b) a slight solubility of the catalyst in water;

(c) the loss of free radicals by the drop, e.g., by solution or chain transfer:

(d) incomplete isolation of the drops.

Furthermore if the reaction is to be suppressed, it is necessary that the volume or weight average of drop size should be below the limit for the particular monomer. This is normally much larger than the number average.

At present, the small amount of published evidence suggests that the reaction rate of benzoyl peroxide catalyzed polymerizations is increased when the system is finely dispersed. For instance, Hohenstein and Mark (23) report that when styrene was dispersed with this catalyst in large drops (e.g., 2 mm.) the reaction was essentially one of bulk polymerization, but that with the smallest drops (0.1 mm. and less) some increase in the rate of polymerization can be observed. Furthermore, with emulsified systems of the same type, Rutovski and Pazinin (24) found that the molecular weight of methacrylate and styrene polymers was greater than in the corresponding bulk polymerizations. Thus, these experiments give no evidence of the effects predicted when active centers are formed in pairs in a finely dispersed system, and it seems doubtful if such conditions can be realized in practice.

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Synopsis

It has been shown that subdivision of certain homogeneous polymerizing systems into droplets of diameter 10^{-4} to 10^{-5} cm. will entail a probability of finding only one active chain in each particle if the kinetics of the reaction remained otherwise unaffected. Some cases of polymerization in compartmentalized systems have been considered, and it has been shown that, where active centers are generated singly within completely isolated drops, the effect of increasing subdivision would be to increase the rate of reaction and chain length. On the other hand, with the formation of active chains in pairs, the opposite effect is to be anticipated, namely a decreasing rate of reaction with increasing subdivision. These conclusions are briefly considered in relation to the problem of dispersion polymerization, and it is shown that the theory of compartmentalization could account for the occurrence of high rates of reaction and chain lengths in the emulsion process, as compared with a bulk system. On the other hand, there is no evidence showing that the reaction rate is ever reduced in finely dispersed systems.

Résumé

On a montré que la division de certains systèmes homogènes polymérisants en gouttelettes d'un diamètre de 10^{-4} à 10^{-5} cm. doit entrainer la probabilité de trouver seulement une chaîne active dans chaque particule, si la cinétique de la réaction n'en est pas modifiée. Certains cas de polymérisations en systèmes compartimentés sont considérés; si les centres actifs sont formés isolément au sein d'une gouttelette complètement isolée, l'effet d'une division croissante sera d'accroitre la vitesse de réaction, ainsi que la longueur de chaîne. D'autre part, en cas de formation de chaînes actives par paires, l'effet opposé doit être attendu, savoir une diminution de la vitesse de réaction avec division croissante. Ces conclusions ont été considérées en rapport avec les problèmes des polymérisations en système dispersé; cette théorie de la compartimentalisation peut rendre compte de vitesses de réactions élevées dans les polymérisations en émulsion, comparées aux polymérisations en bloc. D'autre part, il n'est pas certain, que la vitesse de réaction est toujours réduite par une dispersion fine du système.

Zusammenfassung

Es wird gezeigt, dass die Teilung gewisser homogener Polymerisationssysteme in Tropfen von einem Durchmesster zwischen 10^4 and 10^{-5} cm. es wahrscheinlich macht, dass sich in jedem Teilchen nur eine aktive Kette befindet, falls die Kinetik der Reaktion sonst unveränder bleibt. Einige Fälle von Polymerisation in zerteilten Systemen werden untersucht, und es wird gezeigt, dass dort, wo aktive Zentren in total isolierten Tropfen einzeln gebildet werden, eine Erhöhung des Zerteilungsgrades eine Beschleunigung der Reaktion und Erhöhung der Kettenlänge zur Folge hat. Andrerseits, falls aktive Ketten paarweise gebildet werden, sollte die gegenteilige Wirkung erzielt werden nämlich eine Verlangsamung der Reaktion mit steigender Zerteilung. Diese Schlüsse werden für die Dispersionspolymerisation untersucht und es wird gezeigt, dass die Theorie der Zerteilung die hohen Polymerisationsgeschwindigkeiten und Kettenlängen in Emulsionsprozessen im Vergleich mit Massensystemen erklärt. Andrerseits gibt es keine Evidenz aus der man schliessen könnte, dass die Reaktionsgeschwindigkeit in fein zerteilten Systemen abnimmt.

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Polydispersité de la Cellulose de la Pâte de Bois

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INTRODUCTION

Nous avons été amenés, pour les besoins de nos fabrications de viscose et d'acétate, à étudier la question de la polydispersité de la cellulose contenue dans la pâte de bois.

Outre que du point de vue purement théorique, les auteurs ne sont pas encore d'accord, nous avons rencontré beaucoup de difficultés pratiques, en voulant adapter les méthodes mises au point et valables pour de la cellulose presque pure, telle que celle provenant du coton, à la detérmination de la répartition des chaînes cellulosiques contenues dans les pâtes de bois, d'origine, de nature, de composition et de destination fort différentes.

Nous avons été étonnés, à plusieurs reprises, de constater à quel point pouvaient différer les diagrammes de répartition de longueurs de chaînes de deux lots de pâte, faisant partie d'un même arrivage, du même fournisseur, mais provenant de deux cuiseurs différents. Nos fabrications ayant pour résultat constant et obligé, un clivage des chaînes, il était donc très important pour nous d'étudier, aussi loin que possible:

1. La répartition des chaînes dans le matériau de départ;
2. L'évolution de cette répartition au cours de nos fabrications;
3. L'influence de cette répartition sur les qualités mécaniques de nos produits finis.

On connait à l'heure actuelle, plusieurs méthodes de fractionnement des solutions de hauts polymères et de détermination de leurs poids moléculaires. La plupart de ces méthodes sont encore insuffisantes, soit du côté theorique, soit du côté pratique.

Notre but étant bien défini: adapter les méthodes de laboratoire purement scientifiques à des besoins et à des buts purement techniques, nous avons choisi la méthode par précipitation fractionnée (1) qui, à l'heure actuelle, semble être la plus sûre et la plus simple et par conséquent, la plus facile à appliquer dans un laboratoire de fabrication. Une fois les fractions obtenues, nous en recherchions les poids moléculaires par viscosimétrie.

Nous avons cherché à mettre au point une méthode pratique, simple et dont, surtout, les résultats seraient parfaitement reproductibles, ce qui n'est malheureusement pas vrai, dans le domaine de la cellulose et des ses dérives, de la plupart des méthodes préconisées par la littérature.

On sait, en effet, que la cellulose, comme telle, n'est pas soluble. Il faut s'adresser à un de ses dérives pour arriver à la mettre en solution. Encore faut-il que la préparation de ce dérive ne change en rien la longueur initiale de ses chaînes. Il existe pour cela, deux procédés connus: l'acétylation par l'anhydride acétique en présence de pyridine (2) ou bien la nitration par l'acide nitrique en présence d'acide et d'anhydride phosphoriques (3).

La première de ces méthodes est bonne, mais fort longue. Nous avons préferé adopter la seconde qui est plus rapide, tout en présentant les mêmes garanties de sécurité. Elle donne un produit soluble dans l'acétone.

I. La Nitration

Après bien des essais comparatifs, nous avons constaté que, seul, le mode opératoire suivant, ne provoquait pas de dégradation apparente de nos échantillons:
On prépare 500 g. d'acide phosphorique à 89%. On y ajoute 300 g. d'anhydride phosphorique. Cette quantité est légèrement supérieure a celle qui serait théoriquement nécessaire. Cet excès est destiné à neutraliser l'eau que contient encore l'échantillon de pâte que l'on ne seche pas préalablement. Dans le mélange d'acide et d'anhydride phosphoriques, on verse, en maintenant la température en-dessous de 20°, 700 g. d'acide nitrique (densité = 1.52). On effiloche, à l'aide de deux pointes d'acier, 10 g. de pâte brute. On y ajoute le mélange nitrant, à une température de 4° maximum. On agite pendant une heure, en maintenant la température à 20°. On verse alors le tout sur un creuset Iena G II. On lave sur le filtre avec une solution d'acide acétique à 50%. On achève le lavage en reprenant, plusieurs fois, la nitrocellulose et en l'agitant dans de l'eau distillée, jusqu'à neutralisation complète. Sans séchage intermédiaire, on stabilise au méthanol, à une température de 20°. (On prend soin de récupérer la faible partie de chaînes les plus courtes qui sont déjà solubles dans le méthanol). On sèche en envoyant sur le produit, pendant 30 minutes, un courant d'air sec à la température du laboratoire. On achève le séchage, en maintenant la nitrocellulose pendant 15 minutes, sous un vide de 10 cm. Hg à la température ambiante.

Les échantillons de nitrocellulose ainsi préparés et maintenus secs, se conservent pendant des mois, sans aucune altération.

Le degré d'estérification est mesuré suivant les méthodes habituelles (13.3% d'azote).

II. Dissolution de la Pâte dans la Cupriéthylène Diamine

Qu'elle soit destinée à un traitement alcalin (fabrication de la viscose), ou qu'elle soit destinée à un traitement acide (fabrication de l'acétate), la cellulose subit, dans l'un et l'autre cas, une dégradation plus ou moins profonde suivant les conditions du traitement.

La dégradation est due à la rupture de liaisons de deux natures différentes. Il y aura, d'une part, rupture des liaisons glucosidiques (liaisons fortes) et d'autre part, rupture de liaisons que de nombreux travaux récents et notamment ceux de Pacsu (4) ont montré être beaucoup plus faibles et beaucoup plus sensibles que les premières aussi bien en milieu acide qu'en milieu alcalin.

La nature et la répartition de ces liaisons faibles peuvent différer profondément d'un échantillon de pâte à l'autre suivant leur origine ou le mode de traitement qu'ils auront subi chez le fabricant. Il était donc important pour nous d'essayer de chiffer les différences de comportement des divers échantillons de pâte dans le domaine des liaisons faibles et uniquement dans celui-là. En effet, au cours de nos fabrications, ce sont, évidemment, les liaisons faibles qui se briseront en premier lieu. Cette rupture viendra, en quelque sorte, se superposer au phénomène principal: la rupture des liaisons glucosidiques fortes qui est le fondement même de stades importants de nos fabrications. Le diagramme de polydispersité de la pâte brute ne pouvait nous donner aucun renseignement à ce sujet, puisque la méthode de nitration avait été soigneusement étudiée en vue de rompre le moins de liaisons possible.

On sait, après les travaux de Staudinger et Husemann, que la liqueur de Schweizer rompt pratiquement les liaisons faibles de la cellulose dans la pâte de bois.

Cependant, après les travaux de Strauss et Levy (5), nous avons préféré employer la cupriéthylène diamine, car la cellulose dissoutes dans ce corps, est beaucoup moins sensible à la dégradation oxydative.

Toutefois, la préparation de la cupriéthylène diamine doit se faire avec beaucoup de précautions.

Il est nécessaire de partir de sels de cuivre, d'ammoniaque et de soude tres purs. Habituellement, une quantité plus ou moins grande d'hydroxyde cuivrique reste insoluble. On ne peut pas cependant ajouter un excès d'éthylène diamine pour dissoudre complètement l'hydroxyde. En effet, les chiffres ci-dessous, résumant nos essais, montrent qu'un excès de base organique dégrade la cellulose.

Poids moléculaires	Sans excès d'éthylène diamine	Avec excès d'éthylène diamine
< 75,000	59%	72%
75,000 à 150,000	19%	24%
> 150,000	22%	4%

La difficulté de dissoudre l'hydroxyde cuivrique est due, uniquement, à la trop grande viscosité du milieu. Il suffit d'ajouter au mélange, sous azote, de l'eau jusqu'à obtenir une solution de normalité en Cu^{++} inférieure à 2.

D'autre part, on doit saturer le mélange en $Cu(OH)_2$. Comment procéder, dès lors, pour que le liquide de la couche supérieure, aît une composition correspondant à la formule du complexe tout en ayant une concentration en Cu^{++} d'une normalité égale à l'unité, par exemple.

a. On commence par titrer les ions Cu^{++} du liquide.

b. On titre ensuite, par acidimetrie, la somme: $Cu(OH)_2$ + éthylène diamine.

c. De ces deux titrations, on déduit la teneur des deux constituants du complexe et on determine combien il faut encore ajouter d'éthylène diamine pour que le rapport: ethylene diamine/hydroxyde cuivrique, soit égal à 2.

d. Connaissant la teneur en Cu^{++} du liquide, on ajoute enfin, au mélange, sous azote, la quantité d'eau nécessaire pour obtenir la liqueur standard à 1.0 en Cu^{++}.

En possession de cette liqueur standard, dûment contrôlée, on disperse 10 g. de pâte dans 500 cc. d'eau. On y ajoute 500 cc. de cupriéthylène diamine 1.0 N en Cu^{++}, sous azote purifié. La dissolution est finie en quelques minutes.

On précipite au moyen d'une solution d'acide acétique à 50%. On filtre sur Jena G II et on lave à l'eau distillée, jusqu'à disparition du cuivre. On finit le lavage à l'alcool, puis à l'éther. On sèche, d'abord, par un courant d'air sec pendant 30 minutes à la température du laboratoire, puis sous un vide de 10 cm. Hg pendant 15 minutes à la température du laboratoire.

Cette technique particulière du séchage s'est révélée absolument necéssaire, afin de vaincre la difficulté contre laquelle s'etaient heurtés beaucoup de chercheurs. Il existe d'ailleurs un travaîl de Staudinger et Daumiller (6) qui conclut nettement au fait que le séchage conditionne la solubilité de la nitrocellulose dans l'acétone.

On s'apercoît, en effet, que, pour un séchage poussé de la pâte (plusieurs heures à 105°), une fraction plus ou moins importante de la nitrocellulose, fabriquée à partir de cette pâte, reste insoluble dans l'acétone. On obtient des parties plus ou moins cornées qui refusent de se dissoudre. Ipso facto, le diagramme de répartition de longueurs de chaînes perdait toute signification.

Un séchage progressif et moins brutal, tel que celui que nous effectuons, n'offre pas cet inconvénient. Nous avons établi jusqu'à présent, plus de 100 diagrammes de répartition de longueurs de chaînes et toujours nous avons réussi, grâce à cette technique de séchage, à dissoudre intégralement la nitrocellulose dans l'acétone.

Lorsque l'on sèche brutalement une cellulose hydratée, on élimine non seulement l'eau adsorbée (ce que l'on est convenu d'appeler: le pourcentage d'humidité), mais on élimine également, en tout ou en partie, l'eau fixée, par liaisons hydrogène, sur les groupes hydroxyles libres de la cellulose. Le départ de ces molécules d'eau libère les groupes hydroxyles tout en laissant disponibles des valences secondaires. Ces valences secondaires libérées, vont pousser les chaînes voisines à se réunir. Il en résultera des agglomérats de plus en plus compacts qui, après nitration, resteront pratiquement insolubles dans l'acétone.

III. Le Fractionnement

On dissout 5 g. de nitrocellulose dans un litre d'acétone. Comme liquide précipitant on se sert d'eau.

Les dernières fractions demanderaient de trop grandes quantités d'eau pour être précipitées. On les obtient par évaporation sous vide, sous agitation. Le résidu de ces dernières fractions s'obtient par séchage sous vide poussé.

Nous obtenons toujours, en travaillent ainsi, entre 15 et 20 fractions.

IV. Dégradation Des Solutions Acétoniques De Nitrocellulose

Dès le debut de nos travaux, nous nous sommes heurtés à une grosse difficulté: nous nous sommes aperçus que la nitrocellulose subissait, en solution dans l'acétone, une dégradation profonde. Certains auteurs en parlent, d'autres n'en parlent pas et n'en tiennent pas compte.

Qu'entendons-nous exactement par dégradation? Les faits suivants l'expliqueront:

Un échantillon de cellulose est nitré et stabilisé. Nous avons vérifié qu'à l'état sec, il se conserve sans que se modifient ni son taux d'azote, ni son degre de polymérisation.

On trouvera ci-dessous (Tableau I), prises au hasard parmi nos nombreux essais, deux séries expérimentales. Nous nous sommes servis, pour ces essais, d'une bonne pâte de sapin suédoise, pour viscose. La solution de nitrocellulose dans l'acétone avait 1 g. au litre et était conservée à une température voisine de 20° dans des flacons Pyrex, à l'abri de la lumière.

TABLEAU I. Dégradation de la Nitrocellulose dans l'Acétone

Série III		Série IV	
Nombre de jours	DP	Nombre de jours	DP
0	810	0	850
2	780	3	810
5	700	6	790
8	650	13	710
15	550	18	650
20	500	27	570
29	410	-	-

Les fractions subissent individuellement une dégradation semblable. Le Tableau II en donne un exemple. Il s'agit d'une nitrocellulose fractionnée, faite à partir de la même pâte de bois. Les solutions avaient, suivant les quantités à notre disposition de 0.11 g. à 4.14 g. par litre.

Ces premiers résultats nous ont montré toute l'importance qu'il fallait attacher à ce phénomène. Certains auteurs n'en parlant pas ou l'ayant négligé, nous avons creusé davantage, le problème.

D'après Grevy (7), qui a travaillé sur de la cellulose de coton, l'alcalinité du verre dans lequel la solution est conservée, accèlère la dégradation. Nous avons vérifié que ce phénomène se produit aussi pour de la cellulose de pâte de bois. Le Tableau III donne les résultats de trois séries d'essais sur des solutions à 1 g./litre de nitrocellulose conservées dans des flacons de verre ordinaire à une température de 20°.

Nous avons vérifié également l'influence de la concentration, en essayant une solution dix fois moins concentrée. On verra, d'après le Tableau IV que, placée dans les mêmes conditions, la nitrocellulose en solution acétonique à 0.1 g./litre se dégrade de la memê façon qu'une solution à 1 g./litre.

La température devant probablement jouer un rôle dans ce phénomène, nous avons aussi vérifié son influence. On verra, d'après le Tableau V que l'augmentation de la température, en passant de 20 à 60° n'a d'autre effet que d'accélérer l'apparition d'un palier.

Par contre, on verra d'après la Tableau VI, qu'un refroidissement à 4° est pratiquement sans effet. Les résultats sont les mêmes qu'à 20°.

On pouvait maintenant se demander si la dégradation avait la même intensité sur les grandes chaînes que sur les chaînes courtes. Le Tableau II, que nous avons donné plus haut, ne traduisait que l'ensemble du phénomène. Nous avons fractionné un échantillon de nitrocellulose et mesuré la dégradation sur la partie non fractionnée et sur différentes fractions. On verra, d'après les résultats groupés dans le Tableau VII que le pourcentage de chute est sensiblement du même ordre de grandeur, quelque soit le dégré de polymérisation de la fraction.

TABLEAU II. Dégradation de la Nitrocellulose Fractionnée

Fractions	Nombre de jours	DP	Fractions	Nombre de jours	DP
1	0	1660	12	0	320
	1	1450		10	250
	11	910			
3	0	1500	14	0	290
	10	620		9	200
5	0	710	15	0	270
	10	470		10	170
				25	150
8	0	420	18	0	76
	10	280		8	71

Nos essais personnels nous ont donc convaincus que la nitrocellulose en solution acétonique se dégradait rapidement et profondément au bout de quelques jours. De nombreux auteurs et non des moindres semblent négliger systématiquement ce phénomène. Heureusement, nous en avons trouvé beaucoup d'autres qui l'avaient observé. Nous n'avons pas l'intention de passer en revue tous leurs travaux et nous nous contenterons de renvoyer le lecteur aux travaux personnels et à l'excellent résumé que Spurlin fait de la question dans le traité de Ott ("Cellulose and Cellulose Derivatives," p. 886). Il est arrivé à la conclusion suivante: "As a result of these observations, it appears very likely that the degradation of nitrocellulose is a chain reaction catalyzed by bases,..."

Quelques lignes plus loin, Spurlin ajoute:

"The base- and solvent-catalyzed degradations of nitrocellulose in solution thus appear to be internal oxydation-reduction reactions involving scission of the chain."

Ces observations sont en contradiction avec l'hypothèse de Mathieu (8).

Nous abordons ici une question qui a été fortement discutée ces dernieres années: Les dérivés cellulosiques existent-ils, en solution diluée, à l'état de micelles ou à l'état de chaînes individuelles?

D'après Mathieu, le dérivé cellulosique en solution formerait des paquets de molécules ou micelles gonflées par le solvant. Par repos, il y aurait tendance à la séparation des molécules et à leur dispersion. La dispersion serait d'autant plus grande que la solution est plus diluée. Cette dispersion serait loin d'être immédiate, même dans les solutions tres diluées. Il faudrait plusieurs jours pour que l'état d'équilibre soit atteint. La dispersion complète ne serait atteinte qu'après des temps très longs.

TABLEAU III. Dégradation de la nitrocellulose en Solution acétonique Conservée dans un Flacon de verre Alcalin

Nombre de jours	DP		
	I	II	III
0	810	840	850
2	760	-	-
3	-	760	800
4	700	-	-
6	640	680	-
7	-	-	700
9	-	640	-
10	580	-	640
12	520	-	-
14	480	520	560
18	420	460	-
20	380	420	-
26	-	-	380

En d'autres mots, ceci revient à dire que la chute de viscosité, en fonction du temps observée sur les solutions cellulosiques, serait un phénomène purement physique, laissant aux chaînes leur longueur initiale.

Nous ne sommes pas de cet avis.

Il est bien certain, évidemment, que la dissolution complète d'un dérivé cellulosique n'est pas une chose rapide. Mais, déjà en 1932, Staudinger (9) écrivait que chaque molécule de cellulose ou dérivés est libre en solution suffisamment diluée. Si elle s'associe avec l'une ou l'autre de ses voisines, l'agitation thermique brise immédiatement cette association.

TABLEAU IV. Dégradation de la nitrocellulose en solution diluée

Nombre de jours	DP
0	810
6	700
12	600
20	500
30	400

TABLEAU V. Dégradation de la nitrocellulose en Solution à 60°

Nombre de jours	DP
0	850
5	700
10	600
25	300
50	140
75	140
100	140

D'après Spurlin (10), les partisans de la théorie des micelles ont fini par se rallier, à peu près tous, à la conception moléculaire de Staudinger.

TABLEAU VI. Dégradation de la nitrocellulose en Solution, maintenue à 4°

Nombre de jours	DP
0	840
4	780
10	700
14	640
30	470

Dans ces conditions, d'après les divers travaux sur la question et nos nombreux essais personnels, nous croyons pouivor dire

TABLEAU VII. Dégradation d'une Nitrocellulose avant et après Fractionnement

Jours	Dégré de polymérisation									
	Non fractionné		Fraction 2		Fraction 6		Fraction 12		Fraction 15	
	DP	Perte	DP	Perte	DP	Perte	DP	Perte	DP	Perte
0	950		1980		810		420		240	
		29.5%		29.5%		28%		28.6%		29.1%
15	670		1400		530		300		170	
		23.8%		28.5%		24.5%		26.6%		25.9%
30	510		1000		430		220		125	

que la chute de viscosité des solutions acétoniques de nitrocellulose est un phénomène d'ordre avant tout chimique.

La dégradation dont la vitesse peut être grande au début, peut fortement influencer l'exactitude des déterminations faites sans en tenir compte.

Ce qui est malheureusement plus grave, c'est toute méthode de mesure (et par conséquent, tous les résultats de ces mesures) où le rôle principal est joué par une solution acétonique de nitrocellulose, est, a priori, inexacte si la durée de la mesure dépasse quelques heures.

En ce qui nous concerne, nous nous sommes mis à l'abri de ce reproche. Comme on le verra plus loin, nous ne dissolvons notre nitrocellulose qu'au moment de la mesure. La durée des opérations ne dépasse pas deux heures. Nous ne croyons pas qu'un temps aussi court puisse pratiquement influencer nos résultats.

IV. La Mesure de la Viscosité

Nous nous servons d'un viscosimètre du type Ostwald, dans un thermostat à 20° ± 0.02.

D'après Poiseuille, si g est la constante de la pesanteur, h la différence moyenne des niveaux occupés par le liquide dans les deux branches du viscosimètre et ρ la densité du liquide, r le rayon du capillaire, V le volume écoulé pendant le temps t, la viscosité absolue vaudrait:

$$\eta = \frac{\pi r^4 gh\rho t}{8lV} \qquad (1)$$

La viscosité relative d'une solution vaudrait alors:

$$\eta_r = \frac{\rho t}{\rho_0 t_0} \qquad (2)$$

La viscosité intrinsèque devient donc:

$$[\eta] = \lim_{c \to 0} \frac{(\rho t/\rho_0 t_0) - 1}{c} \qquad (3)$$

La viscosité intrinsèque et le poids moléculaire ainsi calculés, seraient alors independants du viscosimètre employé.

La pratique expérimentale démontre cependant le contraire.

On sait, en effet, que trois causes principales d'erreurs sont possibles: la turbulence, le gradient de vitesse et l'accéleration.

On se met assez facilement à l'abri de la première. Quant à la deuxième, Staudinger et Sorkin (11) ont montré que, pour les solutions acétoniques de nitrocellulose, la valeur de l'expression de Kroepelin:

$$G = \frac{8V}{3\pi t r^3}$$

devait être inférieure à 500 pour que l'erreur devienne négligeable.

L'application de la correction d'accélération d'Hagenbach (12) est plus délicate, car elle amène des complications longues et ennuyeuses dans les calculs. C'est sans doute pour cela que certains auteurs la négligent. En faisant cela, ils s'exposent à commettre — comme on le verra plus loin - des erreurs fort importantes. Nous avons tourné la difficulté en opérant et en raisonnant de la façon suivante:

D'après Hagenbach, on a:

$$\eta = \frac{\pi r^4 gh\rho t}{8lV} - \frac{V\rho m}{8\pi l t} \qquad (4)$$

expression dans laquelle m vaut environ 1 dans notre cas.

Appelons η' la viscosité absolue non corrigée de l'erreur due à l'accélération. Nous aurons dès lors:

$$\frac{\eta}{\eta'} = 1 - \frac{V^2}{\pi^2 t^2 g r^4 h} \tag{5}$$

En remplaçant dans l'equation 5, V par sa valeur tirée de l'expression 4, nous aurons:

$$\frac{\eta}{\eta'} = \frac{(1 + A)^{1/2} - 1}{A/2} \tag{6}$$

dans laquelle:

$$A = \frac{\rho^2 r^4 g h}{16 \eta^2 l^2}$$

En moyenne $g = 981$ et les valeurs de ρ et de η sont fixées par le liquide.

La correction ne dépend plus que du rayon du capillaire. Pour l'acétone $\rho = 0.794$ et $\eta = 0.00337$.

La figure I montre alors la correction correspondante.

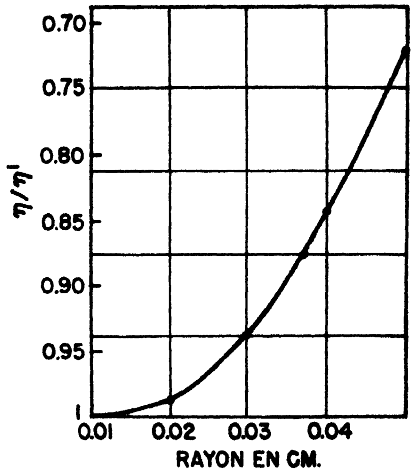

Fig. 1. Variation du rapport η/η' en fonction du rayon capillaire.

Comme $\eta_r = \eta/\eta_0$, nous aurons de nouveau, pour les viscosités relatives corrigées et non corrigées

$$\eta_r/\eta_r' = \eta/\eta' \cdot \eta_0'/\eta_0 \tag{7}$$

En remplaçant dans l'expression 7 les rapports η/η' et η'_0/η_0 par leurs valeurs tirées de l'équation 6 nous aurons:

$$\eta_r/\eta_r' = \eta_r^2 \frac{\rho_0^2}{\rho^2} \frac{[1 + A_0(\rho^2/\eta_r^2\rho_0^2)]^{1/2} - 1}{(1 + A_0)^{1/2} - 1} = R \tag{8}$$

dans laquelle:

$$A_0 = (\rho_0^2/\eta_0^2)(r^4 g h/16\rho^2)$$

Pour les solutions acétoniques, $\rho_0 = 0.794$ et $\eta_0 = 0.00337$.

La figure 2 montre les courbes pour des capillaires différents, de la variation du rapport η_r/η'_r en fonction de la viscosité relative η_r. On peut calculer que pour une viscosité relative égale à 3, le fait de passer d'un capillaire de 0.01 cm. à un capillaire de 0.05 cm. permet une erreur de l'ordre de 31%, si on ne tient pas compte de la correction d'accéleration.

D'après l'expression 2, nous savons que: $\eta_r' = \rho t/\rho_0 t_0$

Dans cette expression, le rapport ρ/ρ_0 est voisin de l'unité pour les solutions assez diluées.

En effet, d'après Jullander (13), le volume spécifique partiel de la nitrocellulose dans l'acétone est égal à 0.569. Comme d'autre part, pour l'acétone $\rho_0 = 0.794$, nous aurons pour une solution de c grammes au litre:

$$\rho/\rho_0 = 1 + 0.000694\,c \tag{9}$$

Dans la figure 3 nous avons mis en courbe les valeurs de la viscosité relative non corrigée en fonction de la viscosité relative corrigée, pour des capillaires différents. La correction à faire apparaît très nettement.

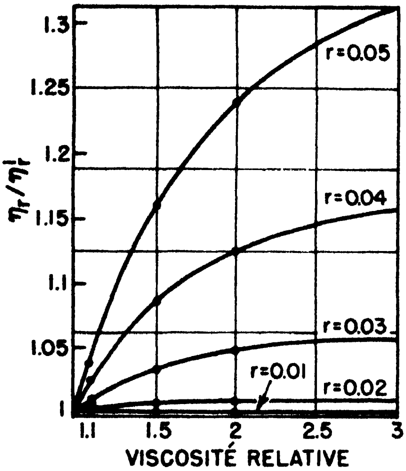

Fig. 2. Variation de la valeur η_r/η'_r en fonction de la viscosité relative corrigée pour différents capillaires.

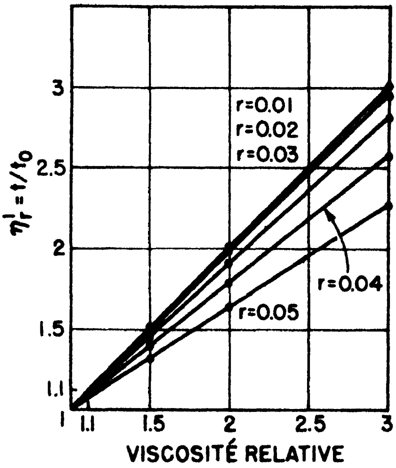

Fig. 3. Variation du rapport t/t_0 en fonction de la viscosité relative corrigée.

La viscosité spécifique corrigée vaut, d'après l'expression 8:

$$\eta'_{sp} = \eta'_r - 1 = \frac{\eta_r}{R} - 1 = \frac{\eta_{sp} + 1}{R} - 1 = \frac{\eta_{sp} + 1 - R}{R} \tag{10}$$

Nous aurons donc, pour les viscosités spécifiques corrigées et non corrigées:

$$\frac{\eta_{sp}}{\eta'_{sp}} = R\,\frac{\eta_{sp}}{\eta_{sp} + 1 - R} = S \tag{11}$$

La figure 4 donne la variation du rapport η_{sp}/η'_{sp} en fonction de la viscosité spécifique corrigée pour différents capillaires. La figure 5 donne la variation de la viscosité spécifique non corrigée, calculée grâce à l'expression $\eta_{sp} = (t/t_0) - 1$ en fonction de la viscosité spécifique corrigée pour différents capillaires.

Il suffira donc de calculer, une fois pour toutes, avant une série d'expériences, les valeurs de R (équation 8) et celles de S (équation 11), pour avoir directement la vraie valeur de η_{sp} en connaissant la valeur expérimentale, $\eta'_{sp} = (t/t_0) - 1$ mesurée sur une solution diluée et le rayon du capillaire.

Pour r = 0.01 cm., on a $\eta'_{sp} = \eta_{sp}$

Pour r = 0.02 cm., $\eta'_{sp} = 0.98\eta_{sp}$

Pour les capillaires de plus large rayon, la correction croît si l'on opère en solution plus diluée.*

Le Tableau suivant donne les valeurs de η'_{sp} correspondant à des η_{sp} de 0.1 à 2 pour des capillaires de rayon 0.03 cm. et 0.04 cm.

	$\eta_{sp} = 0.1$	$\eta_{sp} = 0.5$	$\eta_{sp} = 1$	$\eta_{sp} = 2$
r = 0.03........	0.089	0.451	0.909	1.838
r = 0.04........	0.074	0.380	0.778	1.595

Cette façon de procéder est beaucoup plus simple et beaucoup plus rapide, tout en permettant d'atteindre les vraies valeurs de la viscosité intrinsèque.

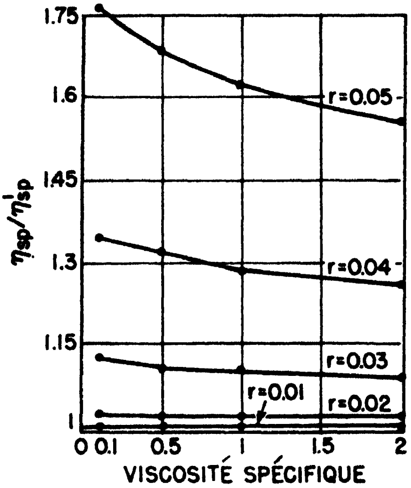

Fig. 4. Variation du rapport η_{sp}/η'_{sp} en fonction de η_{sp} pour différents capillaires.

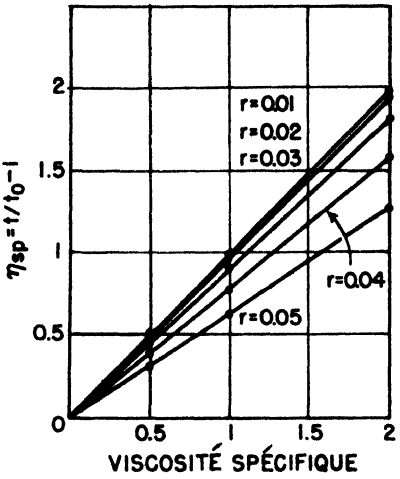

Fig. 5. Variation de la viscosité spécifique non corrigée en fonction de la viscosité spécifique corrigée.

En effet, pour déterminer la viscosité intrinsèque, nous nous sommes servis de la formule de Govaerts et Smets (14):

$$[\eta] = \frac{\eta_{sp}}{c(1 + k_1\eta_{sp} - \eta_{sp}^2/k_2)} \qquad (12)$$

dans laquelle $k_2 = 150$.

Cette formule permet de déterminer les viscosités intrinsèques, même en solution concentrée.

La formule 12 s'applique bien aux solutions acétoniques de nitrocellulose.

L'expression 12 peut s'écrire:

$$1/c = k_1[\eta] + [\eta](1/\eta_{sp} - \eta_{sp}/150) \qquad (13)$$

Ou, en portant dans un diagramme les valeurs de 1/c en ordonnées et les valeurs de la différence $[(1/\eta_{sp}) - (\eta_{sp}/150)]$ en abscisses, nous obtenons une droite.

---

*On en trouvera d'ailleurs la preuve expérimentale dans un travail qui sera publié prochainement dans la revue RESEARCH (London, 1949), "La Viscosité de Structure de la Viscose," par P. Herrent et F. Mouraux.

On détermine aisément η_{sp} et c pour les fractions de nitrocellulose dissoutes dans l'acétone à 20°. La correction de densité, dans le cas de solutions concentrées, se fait grâce à la formule 9. Le graphique de la figure 6 se rapporte à quatre d'entre elles, à titre d'exemple. Nous obtenons des droites. Le fait d'avoir obtenu ainsi des droites nous permet de déduire par l'expression 13 la valeur de k_1 pour une valeur de $[(1/\eta_{sp}) - (\eta_{sp}/150)]$ extrapolée à zero, la valeur de $[\eta]$ moyenne, nous étant donnée par l'inclinaison des droites. Les valeurs de $[\eta]$ se calculent alors par l'expression 12.

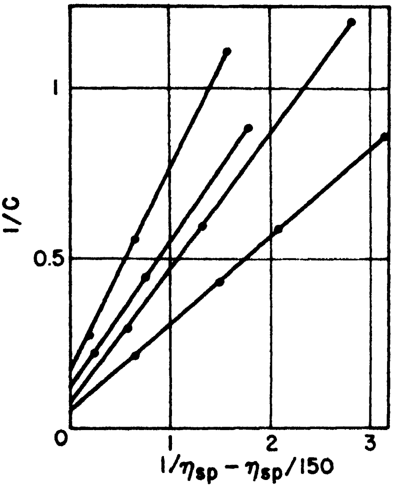

Fig. 6. Détermination de $[\eta]$.

Nous avons constaté expérimentalement que la valeur de k_1 reste la meme pour toutes les fractions d'un même échantillon et pour l'échantillon lui-même non fractionne.

Nous avons procédé de la même façon avec des résultats d'autres auteurs, que nous avons trouvés dans la littérature. Les chiffres de Doyle, Harbottle, Badger, et Noyes (15), recalculés par nous, grâce à l'expression 12, sont traduits en courbe dans la figure 7 et ceux de Jullander (16) dans la figure 8.

On constatera que l'on obtient des droites exactement comme dans la cas de nos propres déterminations. Afin de rendre les chiffres plus explicites encore, nous avons expressément choisi parmi les chiffres de Jullander ceux se rapportant aux solutions concentrées.

D'autre part, en calculant les valeurs de $[\eta]$ par la formule classique:

$$[\eta] = \lim_{c \to 0} \eta_{sp}/c$$

on obtient des chiffres pratiquement comparables à ceux que l'on obtiendrait en calculant l'inclinaison de nos droites.

La bonne concordance que nous avons trouvée entre les chiffres calculés suivant les deux méthodes, nous a confirmés dans la confiance que nous pouvions accorder a l'expression 12.

Toutefois, si les viscosités spécifiques sont inférieures à 1.5, nous nous servons de la formule de Schulz-Huggins:

$$[\eta] = \frac{\eta_{sp}}{c(1 + k\eta_{sp})} \qquad (14)$$

L'exactitude de cette formule simplifiée est suffisante en solution diluée.

D'après Schulz et Blaschke (17), k = 0.315 en moyenne pour la nitrocellulose dans l'acétone.

Comme l'expression 12, la relation 14 permet d'obtenir une bonne valeur de la viscosité intrinsèque, grâce à une seule mesure de la viscosité spécifique.

Si nous recalculons, par la formule 14 par exemple, les résultats de Doyle, Harbottle, Badger, et Noyes (15) et ceux de Jullander (16), on obtient des viscosités intrinsèques, pratiquement semblables pour les solutions diluées où $\eta_{sp} < 1.5$.

La formule 12 nous a donne toute satisfaction, même, et surtout, en solution concentrée.

Toutefois, on corrigera le chiffre expérimental de $[\eta]$ non pas suivant la méthode de Schulz (18), basée sur des approximations qui nous paraissent, pour le moins, discutables, mais en se servant de la méthode que nous avons exposée plus haut.

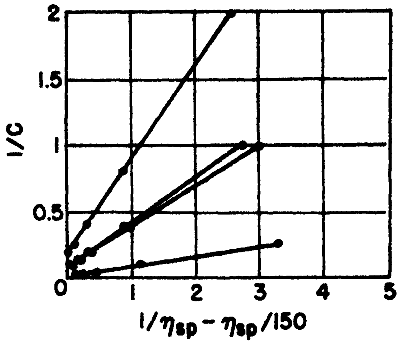

Fig. 7. Détermination de $[\eta]$.

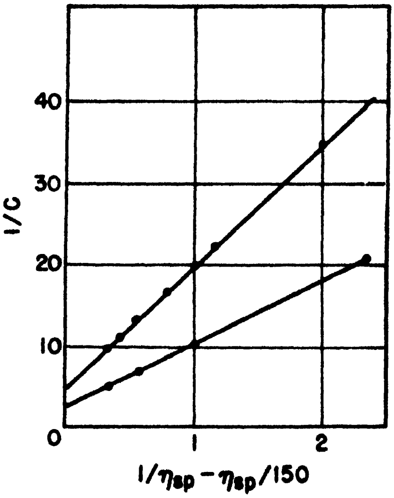

Fig. 8. Détermination de $[\eta]$.

A titre d'exemple, on trouvera dans la figure 9 les courbes provenant d'une pâte de sapin pour viscose. La courbe marquée de cercles a été tracée pour les résultats non corrigés d'un viscosimètre, dont le capillaire avait un rayon de 0.0366 cm. La courbe marquée de croix est celle de la même solution mesurée cette fois (sans correction), avec un viscosimètre dont le capillaire avait un rayon de 0.0301 cm. On remarquera que l'écart est nettement visible.

Dans la figure 10, au contraire, nous avons mis en courbe les mêmes résultats expérimentaux, mais après les avoir corrigés suivant notre méthode.

On remarquera que les cercles et les croix viennent se mettre sur une seule et même courbe avec une exactitude largement suffisante.

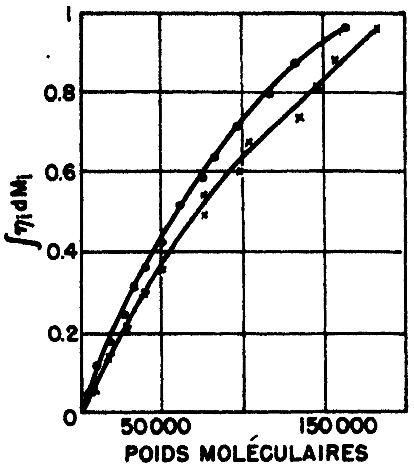

Fig. 9. Polydispersité non corrigée d'une pâte de sapin avec deux capillaires différents.

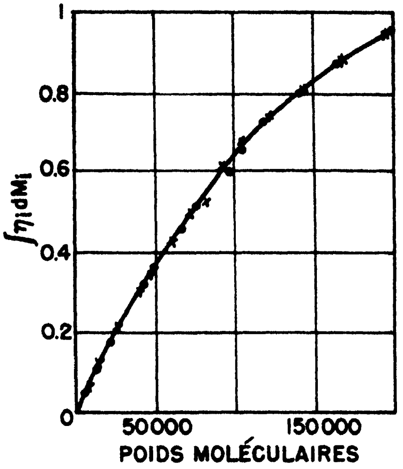

Fig. 10. La même polydispersité corrigée suivant notre méthode.

VI. La Détermination du Poids Moléculaire

Nous avons adopté, pour la détermination des poids moléculaires, la formule classique:

$$[\eta] = kM^{\alpha}$$

Grâce à notre nouvelle méthode de correction, nous étions sûrs de la valeur de $[\eta]$.

Pour trouver les valeurs de k et de α, nous nous sommes livrés à une large revue critique des travaux d'auteurs bien connus (Dobry, Duclaux, Staudinger, Schulz, Mohr, Meyer, Wolff, Wannov, Blaker, Badger, Noyes, Jullander, etc.).

Nous ne pouvons évidemment, reproduire ici ce vaste travail de compilation, nous en donnerons simplement les résultats.

Bien que nous ayions pris la précaution de recalculer les résultats expérimentaux des différents auteurs, afin de ne comparer entre elles que des choses qui soient strictement comparables, on est frappé, après un travail de ce genre, de constater combien est grande la diversité des chiffres auxquels on aboutit et on est obligé de conclure que ces mesures sont encore fort imprécises.

On se rend d'ailleurs fort bien compte que les causes d'imprécision sont sombreuses.

Sans les énumérer toutes, nous citerons notamment: l'hétérogénéité, le degré de nitration, l'origine, le traitement subi par les différents echantillons. Certains auteurs, que nous avons cités plus haut, se sont attachés à définir l'influence de tel ou tel facteur sur la valeur des constantes. A ces différents facteurs, nous en ajouterons un, dont, semble-t-il, on n'a pas mesuré, jusqu'à présent, à sa juste valeur, toute l'importance: la dégradation de la nitrocellulose en solution acétonique.

En attendant de pouvoir faire nous-mêmes, des mesures comparatives (travail en cours), nous avons choisi pour notre cas, la valeur qui nous paraissait la plus probable:

$$k = 10^{-3} \text{ avec } \alpha \text{ égal à } 1.$$

En operant ainsi, nous ne pourrons jamais commettre, éventuellement, qu'une faible erreur, sur la valeur absolue du poids moléculaire.

Nous pourrons d'ailleurs, toujours, si nous désirons avoir des diagrammes qui soient vrais en valeur absolue, les tracer, non plus en fonction du degré de polymérisation, mais en fonction de la viscosité intrinsèque corrigée.

VII. Les Diagrammes

Les méthodes de présentation des résultats de la polydispersité, sont classiques: Connaissant le poids de chaque fraction et leur viscosité intrinsèque, on trace la courbe d'intégration, en prenant comme ordonées l'intégrale $\int n_i d/[\eta]_i$ dans laquelle n_i est la fraction de viscosité intrinsèque $[\eta_i]$ et comme abscisses, la viscosité intrinsèque $[\eta_i']$.

Grâce à la mise au point de détails de la méthode et aux précautions qui se sont révélées absolument necéssaires, ces courbes sont parfaitement reproductibles et trois operateurs différents obtiennent des résultats strictement comparables.

Admettant que $[\eta] = 10^{-3}$ P lorsque les concentrations sont exprimées en gramme de nitrocellulose au litre de solution acétonique, on en déduit la courbe de répartition η_i en fonction de P_i. C'est la courbe en cloche, classique également. Ces courbes en cloches et en particulier leurs maxima étant tres sensibles aux variations, même faibles, de la courbe d'intégration, nous avons préféré employer un mode de présentation discontinu. Nous avons trouvé que cette présentation était plus "parlante" et d'une interprétation plus facile.

Pour les besoins courants de la fabrication, nous avons arbitrairement limité le nombre de fractions dans la représentation graphique. Ayant la courbe d'intégration à notre disposition, nous pouvons, en cas de besoin, multiplier à notre gré, le nombre des fractions rapportées sur le diagramme.

Nous donnons ci-après à titre d'exemple (figs. 11-14), quelques diagrammes de répartition de pâte brute et de pâte traitée à la cupriéthylène diamine.

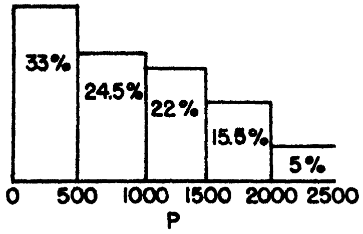

Fig. 11. Pâte brute pour rayonne haute ténacité.

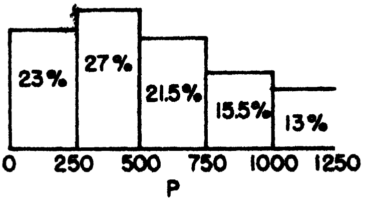

Fig. 12. La même pâte traitée à la cupri.

Il s'agit de pâtes de sapin suédoises, de fournisseurs différents et destinées à des fabrications différentes (viscose, acétate, rayonne haute ténacité, etc.).

Bien qu'il s'agisse dans les deux cas, de pâtes ennoblies, provenant du même fournisseur, on remarquera la différence dans la répartition des chaînes, surtout après le traitement à la cupriéthylène diamine. Ceci n'a rien qui doive nous étonner, étant donné que ces deux pâtes répondent à des besoins différents. Le fabricant de pâte a su conserver à la pâte destinée à la fabrication du fil viscose à haute tenacité, 50% de chaînes d'un degré de polymérisation supérieur à 500. Pour la pâte destinée à la fabrication de l'acétate, la question des longueurs de chaînes pouvait avoir moins d'importance, le but du fabricant étant surtout de nous fournir un matériau soigneusement épuré.

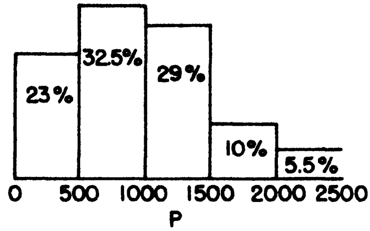

Fig. 13. Pâte brute pour acétate.

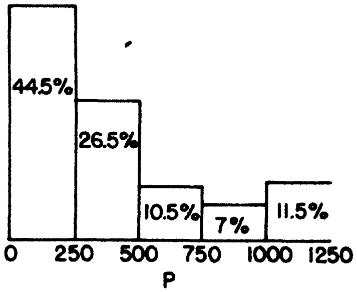

Fig. 14. La même pâte traitée à la cupri.

On remarquera dans la figure 16 que la teneur en chaînes d'un degré de polymérisation supérieur à 1000, est de 5.5%. Nous avons pu établir sur de nombreux échantillons que (toutes autres conditions égales d'ailleurs), les pâtes ordinaires pour rayonne, traitées à la cupriéthylène diamine, dont la teneur en chaîne d'un degré de polymérisation supérieur à 1000, était égale ou inférieure à 5%, se comportaient généralement bien en fabrication.

On verra, par contre (fig. 18), une pâte à 11.5% et (fig. 19), une pâte à 17.5% de chaînes d'un degré de polymérisation supérieur à 1000. Ces deux pâtes se sont très mal comportées en fabrication.

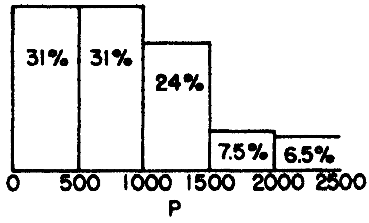

Fig. 15. Pâte brute ordinaire pour rayonne.

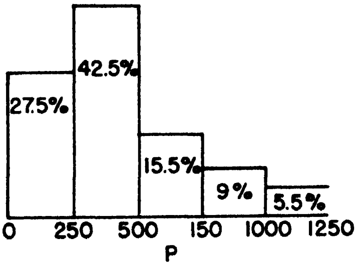

Fig. 16. La même pâte traitée à la cupriéthylène diamine.

Il semblerait que l'on puisse établir une corrélation entre ces deux faits : haute teneur en chaînes très longues et mauvais comportement en fabrication. Notre expérience, dans ce domaine, est encore insuffisante, à l'heure actuelle, pour oser affirmer la chose. Nous ferons remarquer, toutefois, que l'on peut très bien s'expliquer comment une teneur élevée en longues chaînes peut venir perturber dans le sens que nous l'avons observé, une fabrication dont les normes ont été fixées, pour une pâte, à faible teneur en longues chaînes.

Nous poursuivons d'ailleurs nos expériences dans ce sens.

Le diagramme 18 donne la répartition des chaînes dans un fil de rayonne viscose.

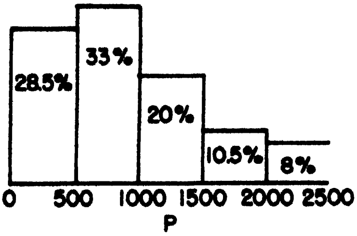

Fig. 17. Pâte brute ordinaire pour rayonne.

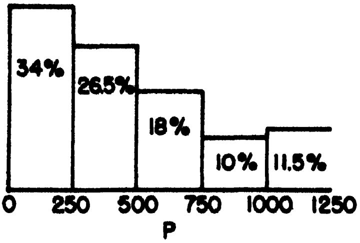

Fig. 18. La même pâte traitée à la cupriéthylène diamine.

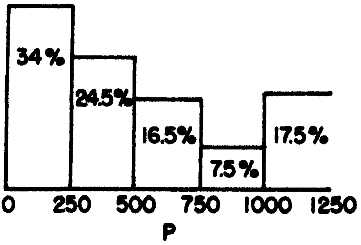

Fig. 19. Pâte ordinaire pour rayonne traitée à la cupriéthylène diamine.

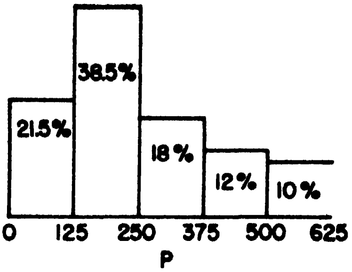

Fig. 20. Fil de rayonne viscose.

VIII. Conclusion

Nous avons cherché à donner plus de précision et ainsi plus d'exactitude aux détails d'une méthode de détermination de la longueur des chaînes d'une cellulose provenant de pâte de sapin. Ces courbes de polydispersité sont actuellement, tout à fait, reproductibles. Nous l'avons fait dans le but d'en tirer des renseignements pratiques pour la fabrication de rayonne viscose et acétate. Nous avons montré, par des exemples, quel genre de renseignements importants on pouvait déjà en tirer.

Nous avons particulièrement insisté sur l'importance qu'il fallait attacher:

1. A la dégradation profonde et rapide que subit la nitrocellulose en solution acétonique.

2. A la correction d'accélération dans les déterminations de la viscosité des solutions acétoniques de nitrocellulose.

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Résumé

Nous avons étudié une méthode pratique et simple, dont les résultats soient parfaitement reproductibles, de détermination de la répartition des longueurs de chaînes de la cellulose provenant de pâtes de bois différentes. Cette méthode nous permettra de mieux comprendre l'influence des différents facteurs de fabrication sur les qualités mécaniques de nos produits finis.

Synopsis

A practical and simple method, with perfectly reproducible results, has been studied for the determination of chain-length repartition of cellulose samples from different wood pulps. By this method, it shall be possible to understand the influence of different factors governing the manufacture and the mechanical properties of our end products.

Zusammenfassung

Eine praktische und einfache Methode, mit ausgezeichnet reproduzierbaren Ergebnissen, zur Feststellung der Verteilung der Kettenlängen von verschiedenen Zellstoffproben wird entwickelt. Mit Hilfe dieser Methode wird es ermöglicht, den Einfluss verschiedener Faktoren, auf die Fabrikation unserer Produkte und deren mechanische Eigenschaften zu verstehen.

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Preparation and Vulcanization of Liquid Polyisoprene Polymers*

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INTRODUCTION

The polymerization of isoprene in bulk to give rubbery polyisoprene of high molecular weight which can be vulcanized to a fairly high quality synthetic rubber has been described by Salomon and Koningsburger (1). If the polymerization is carried out only to low conversions, and particularly in the presence of chain transfer agents (modifiers), liquid polyisoprene of low molecular weight can be produced. In the molecular weight range up to about 1200 these liquid polymers can be readily poured at room temperature. It has been found possible to vulcanize these liquids to rubbers of reasonable physical properties with very slight shrinkage.

In particular, it has been found possible to vulcanize these liquids at room temperature, with dithioladipic acid and dithiolsebacic acid.

The most convenient catalyst-modifier system proved to be tert-butyl hydroperoxide and dodecyl mercaptan. The molecular weight can be controlled by varying the monomer-modifier ratio and the extent of conversion.

In the following pages data on molecular weight as a function of monomer-modifier charge ratio and conversion are presented for the system, isoprene, dodecyl mercaptan, tert-butyl hydroperoxide. Density and viscosity data are given for various molecular weights. Finally, various vulcanization recipes are discussed.

EXPERIMENTAL

Materials

The isoprene used was a commerical grade obtained from Newport Industries, Inc. The isoprene was purified by simple distillation, being collected in the range of temperatures from 33 to 35°C.

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†Present address: Bristol, Pennsylvania.

**The authors wish to thank Dr. Cunneen of the British Rubber Producers Research Association who pointed out the remarkable vulcanizing properties of this substance and who supplied us with a sample.

The dodecyl mercaptan was obtained from Hooker Electrochemical Company. It consisted of a mixture of straight-chain twelve and thirteen carbon mercaptans and was used without purification.

The tert-butyl hydroperoxide and tert-butyl perbenzoate were obtained from the Union Bay State Company and used without purification.

The dithioladipic acid was prepared after the procedure of Sunner and Nilson (2). The crude product was isolated from the ether extract rather than by recrystallization. Dithiolsebacic acid was prepared by the same method starting with sebacyl chloride.

Monsanto plasticizer HB-40, a high-boiling liquid hydrocarbon of the hydrogenated terphenyl type, was used as obtained.

Method

All polymerizations were carried out in bulk in sealed Pyrex glass 25 x 250 mm. tubes. The tubes were charged from two-thirds to three-quarters full, cooled in Dry Ice, sealed in air, and heated in iron pipes in a specially constructed electric heater with the temperature controlled to $\pm 1^{\circ}$C. for the required time. Upon removal from the heater the tubes were cooled in Dry Ice, opened, and monomer removed in one of the two following ways.

In processing single tubes, the contents was poured into a 50-50 mixture of methanol and acetone (500 ml./50 g. monomer) in order to separate the polymer from any unreacted monomer and mercaptan. The polymer precipitated as an oily layer at the bottom. The supernatant liquid was removed by decantation, and the polymer heated at 60-70°C. under an 18-20 mm. vacuum and finally under a 1-2 mm. vacuum until constant weight was obtained. Spot tests for mercaptan on polymers treated in this way gave negative results.

When larger batches were being prepared for vulcanization studies, etc., a different procedure was used for economy of solvent. The contents of the tubes were passed through a steam-heated spiral condenser into a suction filter flask heated in an oil bath at 150°C., the entire assembly being subjected to an 18-20 mm. vacuum. The monomer-polymer mixture was added slowly so that most of the monomer was removed while the mixture was passing through the spiral condenser. After about 6 hours at 18-20 mm., the flask was subjected to a 1-2 mm. vacuum for about 18 hours. Polymers isolated by the first method will be referred to as precipitated polymers; those processed by the second method will be referred to as unprecipitated polymers.

The principal difference between these two methods is that the former removes some of the very low molecular product, so that for a given monomer-modifier ratio the molecular weight is slightly higher and the polymer more viscous when the precipitation method of isolation is used.

The number-average molecular weights were determined cryoscopically in benzene solution. The amount of unsaturation was determined by addition of bromine (3). The sulfur analyses* were performed by the method of Cheyney (4). Viscosities of the liquid polymers were determined with the Brookfield instrument.* Densities were determined by a pycnometer at 20°C.

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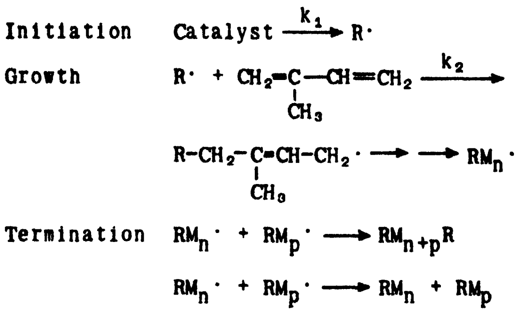
*The authors wish to acknowledge the assistance of Mr. D. C. Kane who performed these analyses.

In a typical run using a 50-1 monomer-mercaptan mole ratio, 75 g. isoprene, 4.65 g. dodecyl mercaptan, and 0.35 g. tert-butyl hydroperoxide were charged in a standard Pyrex tube and heated for 24 hours at 135°C. There was a 65% yield of unprecipitated polymer of cryoscopic molecular weight 1050. The Brookfield viscosity was 50,000 centipoises.

DISCUSSION AND RESULTS

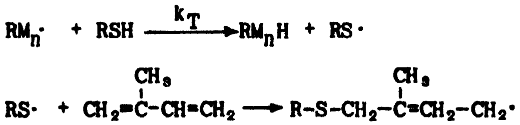
The peroxide-catalyzed polymerization of isoprene proceeds by a radical chain mechanism of the following type:



$$\begin{array}{ll}
\text{Initiation} & \text{Catalyst} \xrightarrow{k_1} R\cdot \\
\text{Growth} & R\cdot + CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH{=}CH_2 \xrightarrow{k_2} \\
 & R{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_2\cdot \longrightarrow \longrightarrow RM_n\cdot \\
\text{Termination} & RM_n\cdot + RM_p\cdot \longrightarrow RM_{n+p}R \\
 & RM_n\cdot + RM_p\cdot \longrightarrow RM_n + RM_p
\end{array}$$

Both 1,4 and 1,2 addition are known to occur in diene polymerization (5). In addition, branching and cross-linking take place by radical addition to unreacted double bonds. As has been recently shown (1), if the conversion is carried out to sufficiently high percentages, cross-linked products will be formed.

Chain transfer agents, such as mercaptans, have been shown to control molecular weight without retarding the rate of reaction by reacting with growing radicals as follows:



$$\begin{array}{l}
RM_n\cdot + RSH \xrightarrow{k_T} RM_nH + RS\cdot \\
RS\cdot + CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{=}CH_2 \longrightarrow R{-}S{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2{-}CH_2\cdot
\end{array}$$

The theory of chain transfer has been developed by several authors (6,7). If the specific rate constants for chain transfer and chain growth are k_T and k_2, respectively, then, at a time when the molar ratio of monomer to transfer agents is (M)/(S), the degree of polymerization of the polymer being instantaneously formed is:

$$k_2(M)/k_T(S)$$

In the case of the polymerization of isoprene in the presence of dodecyl mercaptan, the ratio of k_T/k_2 is larger than unity, so that the mercaptan is used up more rapidly than the monomer, and the degree of polymerization increases with increasing conversion. Cryoscopic molecular weights and per cent conversion at different times are given for various mercaptan-monomer molar ratios in Table I. The con-

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*The authors wish to acknowledge the assistance rendered by the Thiokol Corp. in allowing us the use of their Brookfield viscometer.

TABLE I. Polymerization of Isoprene with Dodecyl Mercaptan (at 100°C)

(S)/(M), precipitated	Time, hours	Per cent Conversion	Cryoscopic mol. wt.	No. double bonds per molecule	No. sulfur atoms per molecule	Theoretical mol. wt.	Loss of unsaturation
	A	B	C	D	E	F	G
1/10	2	7	400	2.8	0.95	390	10
	4	17.5	410	2.8	0.94	390	10
	8	29	410	3.1	0.90	400	10
	24	35	475	3.4	0.99	440	35
1/20	2	12.5	500	3.8	0.99	470	30
	4	19	515	5.1	0.89	530	-15
	8	-	600	5.9	0.83	575	25
	12	36	675	6.5	0.73	595	80
	24	40	775	7.9	0.77	700	75
	48	54	800	8.7	0.64	725	75
1/30	2	7.5	620	5.7	0.99	600	20
	4	17	750	7.6	0.95	720	30
	8	-	760	7.9	0.83	715	45
	12	25	875	9.5	0.83	820	55
	24	40	900	10.3	-	-	-
	48	54	1000	11.6	0.60	915	85
1/40	2	12	800	8.1	0.94	750	50
	4	16	800	8.4	0.87	755	45
	8	19	875	9.6	0.81	825	50
	12	32	925	9.6	0.80	820	115
	24	42	975	11.7	0.74	850	125
	48	59	1050	12.2	0.65	965	85
				Unprecipitated			
1/10	24(110°C.)	53	390	3.0	0.75	365	25
1/20	24(110°C.)	75	630	6.0	0.76	570	60
1/30	24(135°C.)	65	800	9.0	0.52	725	75
1/50	24(135°C.)	60	1050	11.6	0.49	895	155

version is expressed as weight per cent based on the total charge of monomer and modifier. All runs were made at 100°C. with 0.46 weight per cent tert-butyl hydroperoxide as the catalyst.

It is clear from a study of Table I that the precipitation technique removes some of the very low molecular materials beyond those removed by evacuation. This was further verified by extracting the unprecipitated polymers with the same amount of ethanol-acetone mixture that would have been used had they been precipitated. The insoluble precipitated portion of the polymers was brought to constant weight under vacuum and heat. The supernatant liquid was distilled to remove the methanol and acetone and then heated under vacuum. The results are shown in Table II.

TABLE II. Extraction of Polyisoprene with Methanol-acetone

(S)/(M)	Mol. wt.	Per cent soluble	Mol. wt. soluble	Per cent insoluble	Mol. wt. insoluble
1/10	390	47	320	53	450
1/20	630	25	330	75	850
1/30	800	13	390	87	1000

STRUCTURE AND PHYSICAL PROPERTIES

In Table I data are presented on the nature of various polymers as calculated from the sulfur analyses and unsaturation determinations.

The number of double bonds per polymer molecule is calculated from the moles of bromine taken up and the cryoscopic molecular weight according to the formula:

$$\text{Number of double bonds} = \frac{(\text{moles } Br_2)(\text{molecular weight})}{\text{Weight of polymer}}$$

The number of sulfur atoms per polymer molecule is calculated from the amount of sulfur present and the cryoscopic molecular weight according to the formula:

$$\text{Number of S atoms per molecule} = \frac{(\text{Wt. } BaSO_4)(\text{molecular weight})}{(233.4)(\text{Weight of sample})}$$

The results indicate that not every molecule contains a dodecyl mercaptan unit, and the number of sulfur atoms per polymer molecule decreases with increasing conversion.

In column F a theoretical molecular weight is calculated by use of the equation:

$$\text{Theoretical mol.wt.} = 210(\text{No. of S atoms per molecule}) + 68(\text{No. of double bonds per molecule})$$

The difference between this value and the cryoscopic molecular weight should give a measure of the loss of unsaturation in molecular weight units within the limits of the experimental error. This loss can possibly be ascribed to branching, which is known to increase with increasing conversion as does the value for loss of unsaturation determined, or the low sulfur values may be due to chain transfer with the monomer. It is possible that the values in column G are merely the result of experimental error.

Densities were determined for several of the precipitated and unprecipitated polymers as shown in Table III. The densities increase with increasing molecular weight and approach that of natural rubber. The polymers precipitated from methanol-acetone show less spread in the density values over the range of (S)/(M) ratios than do the unprecipitated polymers, indicating that the former are probably more homogeneous than the latter. The densities of squalene (a hydrocarbon composed of 6 isoprene units), dodecyl mercaptan, and natural rubber are included for comparison.

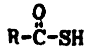
The viscosities of several unprecipitated liquid polyisoprenes at 17°C. as determined with the Brookfield viscosimeter are shown in Table III. When $\ln \zeta$ is plotted against M_n, the cryoscopic molecular weight, a straight line is obtained so that the data fit a relationship of the type: $\ln \zeta = A + BM_n$, where A and B are constants.

TABLE III. Density and Viscosity Measurements

(S)/(M)	Cryoscopic mol. wt.	Density	ζ, centipoises	$\ln \zeta$
1/10 unpptd.	390	0.876	26	3.258
1/20 "	630	0.887	223	5.407
1/30 "	800	0.895	4820	6.178
1/50 "	1050	0.910	50000	10.821
1/10 pptd.	525	0.888		
1/20 "	650	0.893		
1/30 "	825	0.896		
1/50 "	1400	0.905		
Squalene	408	0.864		
Dodecyl mercaptan	210	0.845		
Natural rubber	-	0.92		

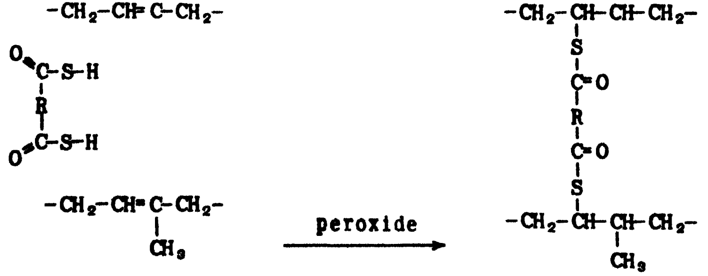
VULCANIZATION

It has been found (10) that thiol acids of the general formula:



$$R-\overset{O}{\overset{\|}{C}}-SH$$

add to the double bonds of olefins and rubber in an anti-Markownikoff addition in the presence of peroxides. In a like manner, cross-linked products can be obtained with dithiol acids and the liquid polyisoprenes presumably as follows:



Both dithioladipic acid and dithiolsebacic acid have been prepared and used in vulcanizing the liquid polyisoprene polymers. It has been found that polymers of about 700 molecular weight are the lowest that can be cured to a rubberlike material. The dithiol acids are not compatible with the liquid polymers, but by dispersing the acids in an equal weight of HB-40 plasticizer prior to addition to the liquid polymer, a clear or translucent product is obtained. Various peroxides were tried, the most satisfactory being tert-butyl perbenzoate, since it gave the longest working life and still gave a good cure at room temperature. All nonreinforced vulcanizates so far obtained have low tear resistance and low tensile strength.

The standard amount of dithiol acid for purposes of cross linkage was taken to be one molecule of dithiol acid per two polymer molecules. It was found that smaller amounts down to 0.6, the standard amount, do give vulcanized products. With larger than the standard amount of dithiol acid, the products are much more tightly cured, with consequent increase in hardness and decrease in tear resistance. The best cures so far obtained have been with the standard amount of dithiol acid and 1% (by weight) of peroxide (based on the liquid polymer) for 24 hours at 100°C. With larger amounts of peroxide (about 5%) cures can be obtained in about one-half hour at room temperature, but the products darken considerably on aging in a circulating air oven at 100°C., whereas the polymers cured with a small amount of peroxide at 100°C. are much more stable to heat aging. Various vulcanization formulae and Shore hardness measurements are given in Table IV.

TABLE IV. Vulcanization of Polyisoprenes

	A	B	C	D	E	F	G	H	I
Polyisoprene (1100 mol. wt.)	100	100	100	100	-	-	100	100	100
(900 mol. wt.)	-	-	-	-	100	-		-	-
(750 mol. wt.)	-	-	-	-	-	100	-	-	-
Dithiolsebacic acid	6.4	10.6	21.2	13.3	13.3	13.3	-	-	-
Dithioladipic acid	-	-	-		-	-	20	10	20
HB-40	6.4	10.6	21.2	13.3	13.3	13.3	20	10	20
tert-Butyl perbenzoate	2	2	2	2.75	2.75	2.75	1	2	20
Time of cure, hours	2	2	2	1	1	1	18	2	0.5
Temperature, °C.	100	100	100	100	100	100	100	25	25
Shore hardness	1	11	23	7	2	1	14	1	10

Summary

1. Liquid polyisoprene can be prepared by peroxide-catalyzed bulk polymerization in the presence of chain transfer agents such as mercaptans.

2. The molecular weight of the liquid polymers may be regulated by varying the ratio of monomer to mercaptan and the extent of conversion.

3. These polymers have been characterized as to molecular weight, unsaturation, sulfur atoms per molecule, "Brookfield" viscosity, and density.

4. These polymers can be vulcanized to give rubberlike products by a peroxide-catalyzed reaction with dibasic thiol acids.

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Synopsis

By means of chain transfer agents such as dodecyl mercaptan, polyisoprenes whose number-average molecular weights range between 300-1200 and which are liquid at room temperature have been prepared. The structure and physical properties of these substances have been investigated. Vulcanization of these liquids to rubberlike materials at room temperature and above is described.

Résumé

Au moyen de produits provoquant des transferts de chaîne, tel le mercaptan dodécylique, on a préparé des polyisoprènes liquides à température de chambre, et dont le poids moléculaire moyen est compris entre 300-1200. La structure et les propriétés de ces substances ont été examinées. La vulcanisation de ces liquides, en un produit élastomère, à température de chambre et au delà, est également décrite.

Zusammenfassung

Durch Modifikatoren wie zum Beispiel Dodecylmerkaptan wurden Polyisoprene mit Zahlendurchschnitts-Molekulargewichten zwischen 300 und 1200 hergestellt die bei Raumtemperatur flüssig waren. Die Struktur und physikalischen Eigenschaften dieser Substanzen wurden untersucht. Die Vulkanisierung dieser Flüssigkeiten zu gummiartigen Stoffen bei Raum- und höherer Temperatur wird beschrieben.

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Change in Crystallinity upon Heterogeneous Acid Hydrolysis of Cellulose Fibers*

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INTRODUCTION

It has long been known that the sorptive capacity for water vapor of cellulose fibers tends to decrease upon treatment with acids in the preparation of "hydrocelluloses." It has also been suggested more than once that the percentage of crystalline matter would increase in this procedure.

Recently, Nickerson and Habrle (1) published experiments on the treatment of various cellulose fibers with boiling 2.5 N sulfuric acid. They followed the loss in weight with time of the fibers and determined the matter going into solution in the form of glucose. The sum of the two figures yielded the initial weight of the material within 1%. They found a rapid drop of the sorptive capacity within the first 20-30 minutes of hydrolysis. After that the sorptive capacity remained almost constant for a considerable period of time and showed a slight increase after prolonged hydrolysis. In conformity with other authors, they also found a rapid drop in cuprammonium viscosity of the residual fibers within the first 15 minutes of hydrolysis. Upon further hydrolysis the viscosity remained practically constant, corresponding to a DP of 250-280 in native fibers and 110-130 in rayon.

Nickerson and Habrle believe that the fibers contain a small quantity of amorphous cellulose which is very hygroscopic and which is attacked first upon boiling with the acid. The rapid drop in sorptive capacity would correspond to the removal of this portion. Upon further hydrolysis only the surface of the crystallites would be attacked and this would no longer affect the sorptive capacity.

This explanation seems to be very improbable. Since it was observed, for instance, that rayon with an initial regain of 11.9% (at 65% R.H.), after having lost 5.6% in weight, exhibited a regain of 8.6%, this would mean that 5.6% of amorphous substance would absorb 3.3% water or 59 parts of water per hundred. There is no support for such an extravagant assumption.

The present paper deals with crystallinity measurements according to our recently published x-ray method (2,3) as applied to rayon and ramie fiber hydrolyzed according to the recipe given by Nickerson and Habrle. The results show that upon boiling with 2.5 N sulfuric acid the amount of crystalline substance in rayon rapidly increases from about 40% to about 50% within the first half hour, and remains constant upon further hydrolysis. In ramie, no crystallinity change could be observed within experimental error.

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*Communication No. 60 from the Institute for Cellulose Research of the AKU and affiliated Companies, Utrecht, Netherlands.

EXPERIMENTAL

A commercial staple fiber and purified ramie fibers were boiled with 2.5 N sulfuric acid, according to the recipe of Nickerson and Habrle, for 1/2, 1 1/2, and 4 hours. After 4 hours the fiber (particularly the viscose fibers) were already highly disintegrated so that it seemed inadvisable to investigate longer periods of hydrolysis.

The regains observed (upon absorption) at 65% R.H. are listed in Table I together with the loss in weight of the samples. The latter data were taken from the paper by Nickerson and Habrle (1) for viscose rayon and cotton linters (assuming that ramie behaves like cotton in this respect).

TABLE I. Observed Regain and Loss in Weight Dependent upon Time of Hydrolysis.

Time of hydrolysis, hours	Viscose Fibers		Ramie Fibers	
	Regain, %	Loss in wt., %	Regain, %	Loss in wt., %
Blank	13.5	-	7.0	-
1/2	10.9	5.6	6.1	2.0
1 1/2	11.1	11.4	-	4.6
4	10.5	18.4	6.8	7.2

In Table II the total integrated intensity I_{cr} of the crystalline peaks, the height A_m of the background maximum, and the total in-

TABLE II. Intrinsity I_{cr} of Radiation Diffracted by the Crystalline Portion, Height A_m of Diffuse Background, and Total Diffracted Radiation $I_{tot.}$

Time of hydrolysis, hours	I_{cr}	A_m	$I_{tot.}$
	Rayon		
Blank	110	56	440
1/2	151	43	412
1 1/2	160	41^5	420
4	173	37^5	410
	Ramie		
Blank	202	26	410
1/2	198	24^5	418
4	202	22	394

tensity $I_{tot.}$ of scattered radiation between $2\theta = 7^\circ$ and 42° are given, as derived from the x-ray observations (all reduced to standard conditions).

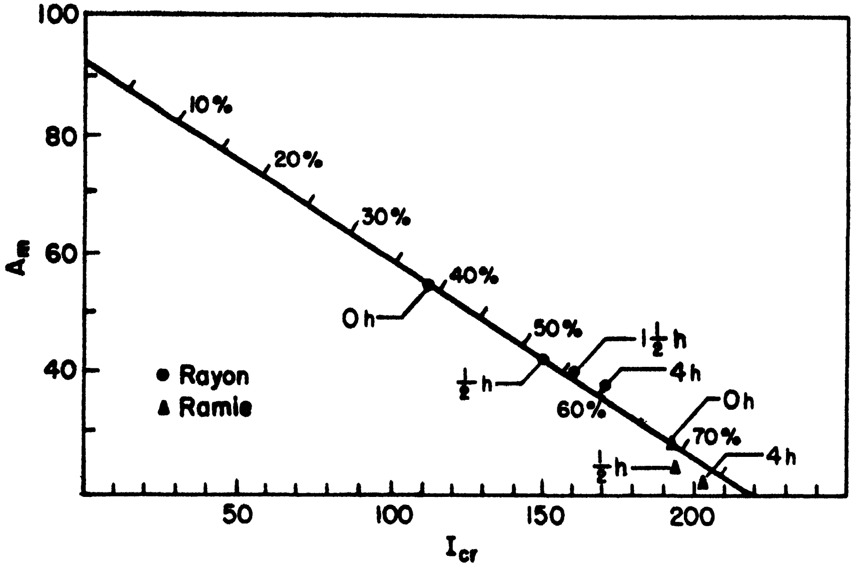

Fig. 1. X-ray data plotted in crystallinity nomogram.

In Figure 1 the results of the x-ray experiments are given in graph form (for which see ref. 3). In Table III the observed crystallinity percentages (x_1) from Figure 1 are listed together with the same values calculated on the weight of the original substance present before hydrolysis (x).

TABLE III. Crystallinity Percentages Found (x_1) and Those Corrected for Loss in Weight during Hydrolysis (x_2)

Time of hydrolysis, hours	Viscose fibers		Ramie fibers	
	x_1	x_2	x_1	x_2
Blank	39	39	69	69
1/2	52	49.5	71	68
1 1/2	56	49.5	—	—
4	60	49.0	73	68

In a previous paper (4) the importance of also evaluating the half-width and the intensity of the two principal equatorial lines in the x-ray photographs separately has been demonstrated. The relevant data are recorded in Table IV.

It is recalled that the half-width values are given in millimeters on the film (at 40 mm. distance from the specimen; pinhole, 0.8 mm.; specimen thickness, 1.6 mm.). The experimental error in these figures amounts to about ±0.1.

The intensity values listed were all reduced to 39% crystalline substance for rayon and to 69% for ramie.

TABLE IV. Half-Width (in Millimeters) and Intensity Values of the Two Principal Equatorial Lines

Time of hydrolysis, hours	Half-width		Intensity	
	A_0	A_3A_4	A_0	A_3A_4
	Viscose Rayon			
Blank	2.5	3.4	0.09_5	0.94
1/2	1.6	3.2	0.04	0.89
1 1/2	1.7	3.0	0.07	0.92
4	1.7	3.2	0.07	0.99
	Ramie			
	A_1A_2	A_4	A_1A_2	A_4
Blank	3.3	2.8	0.58	1.22
1/2	2.9	2.6	0.46	1.12
4	2.5	2.7	0.49	1.20

DISCUSSION

The figures listed in Table III demonstrate that an increase in crystallinity takes place in the viscose fibers within the first half hour of hydrolysis, amounting to 10% of the total cellulose originally present. In ramie no significant change is observed. It also follows from the figures that the substance going into solution comes from the amorphous fraction exclusively, the crystalline fraction remaining unchanged in quantity after completion of the recrystallization.

If we take for granted that the regain of cellulose is approximately proportional to its amorphous fraction (5), then the regain of rayon should drop from 13.5 to 10.6% after 1/2 hour of hydrolysis. The observed figure is 10.9 (see Table I). Upon prolonged hydrolysis this figure should further decrease and reach 9.0% after 4 hours of hydrolysis. This, however, is not corroborated by the observations for reasons not disclosed.

In ramie the observed change in regain is very small, which is again roughly in line with the x-ray data. The figures listed in Table IV show that the half-width and intensity values of the second equatorial line (A_3A_4 in rayon and A_4 in ramie) are unaffected by hydrolysis within experimental error. On the other hand, the first equatorial line is affected.

The half-width of A_0 in rayon diminishes in the first half hour of hydrolysis, indicating that (apart from the increase in total crystalline fraction) a two-dimensional recrystallization (cf. ref. 5) occurs, accompanied (as usual) with a drop in total intensity.

In ramie it is seen that in the course of hydrolysis a sharpening of the first equatorial line also occurs. In this case, this is probably due to a gradual transition of the crystalline portion into Cellulose IV (which is not surprising in view of the high-temperature treatment). In Cellulose IV the lines A_1 and A_2 merge into one single line.

The result of acid hydrolysis, obviously, primarily entails a cutting of chains in the amorphous regions. In rayon fibers, representing an irregular network structure consisting of crystalline regions interconnected by disordered chains, the cutting of part of these chains seems to remove part of the entanglements and insufficient segmental freedom of movement and rotation which prevent further crystallization. This explanation has already been suggested earlier and we think that it is a reasonable one.

It seems significant, however, that no similar effect is observed in ramie, suggesting that the structure of the amorphous fraction in native fibers is of a different nature.

Some authors have recently attempted to base a method for crystallinity determination in cellulose specimens on acid hydrolysis experiments (6). Apart from the fact that chemical methods aiming at the determination of degree of crystallinity are, a priori, likely to yield results with doubtful physical meaning, the present results demonstrate that acid hydrolysis will be particularly unsuitable for such purpose in that the degree of crystallinity may be affected by the reaction itself.

Acknowledgment

The authors are indebted to the Physical Laboratory of the Technical University in Delft for the use of its x-ray equipment.

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Synopsis

The recently developed x-ray method of crystallinity determination is applied to products of heterogeneous acid hydrolysis of cellulose fibers. Upon treatment of viscose rayon fibers with boiling 2.5 N sulfuric acid, the crystalline fraction is increased from 39 to 49% within half an hour, and remains constant upon prolonged treatment. Ramie does not show any change in percentage crystallinity when subjected to the same treatment. Its crystalline fraction is, however, transformed into cellulose IV. The observed changes

in moisture regain of the hydrolyzed products are in line with the x-ray results.

Résumé

La méthode de détermination roentgénographique de la cristallinité, développée récemment, est appliquée aux produits d'hydrolyse acide hétérogène des fibres cellulosiques. En faisant bouillir des fibres de rayonne-viscose dans l'acide sulfurique (2.5 N), la fraction cristalline s'accroît de 39 à 49% en une heure et demie, puis reste constante par traitement prolongé. La ramie soumise à un traitement semblable, ne présente aucune variation dans le pourcentage de cristallinité. La fraction cristalline est, toutefois, transformée en cellulose IV. Les changements observés au cours de l'humidification des produits d'hydrolyse, sont en accord avec les résultats obtenus au moyen des rayons X.

Zusammenfassung

Die neuerdings ausgearbeitete Röntgenstrahlen-Methode für Kristallinitätsmessungen wird auf die heterogene Säurehydrolyse von Cellulosefasern angewandt. Wenn Kunstseidefasern mit kochender 2.5 Schwefelsäure behandelt werden, steigt die kristalline Fraktion innerhalb einer halben Stunde von 39% auf 49% und bleibt dann bei längerer Behandlung konstant. Bei Ramie wird bei derselben Behandlung keine Änderung im Prozentsatz der Kristallinitat beobachtet. Seine krystalline Fraktion wird aber in Cellulose IV verwandelt. Die beobachteten Veränderungen in der Feuchtigkeitswiederaufnahme der Hydrolyseprodukte stimmen mit den Röntgenergebnissen überein.

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Osmometry of High Polymer Solutions. I. Osmometer and Membranes

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INTRODUCTION

In determining number-average molecular weights of high polymers by the osmotic method it is desirable to use an osmometer having cells of a large surface/volume ratio, and fitted with capillaries of fine bore. Along with suitable membranes, such an osmometer can be used to determine osmotic pressures in a reasonably short time by means of a dynamic method.

The type of osmometer designed by Fuoss and Mead (1) is very suitable for work of this kind. In the original design of these authors, however, no provision has been made for thermostating the instrument. This is a major drawback when membranes of permeability lower than denitrated collodion are employed; at low membrane permeabilities there is a considerable thermometer effect in the osmotic cell plus measuring capillary, and temperature control becomes essential. It is also desirable to thermostat the instrument even when fast membranes are used, since measurement of the temperature effect of osmotic pressure is a useful means of determining heats and entropies of dilution in polymer-liquid systems.

Complete immersion of such an osmometer in a water bath is not possible without radical alterations in design, since it is necessary to have some means of manipulating the lower needle valves during the course of a run. Complete immersion also destroys some of the advantages (e.g., ease of membrane replacement) offered by this type of design. In the modified instrument described below, this difficulty has been overcome, and various other improvements in design have been effected.

A MODIFIED FUOSS-MEAD OSMOMETER

The osmometer was constructed of forged "Delta" bronze, the half-cells being spun out of the solid metal according to the Fuoss-Mead pattern. The cells were only 1 mm. deep; otherwise the dimensions were the same as in the original design. To eliminate leakage at the edge of the membrane it was necessary to grind the cell surfaces optically flat on a glass plate. In order to ensure a perfect fit the surfaces were finally lapped very slightly against each other

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in a circular manner, only a few turns being given since the outer edges tend naturally to be ground away more rapidly than the parts nearest the center. With these precautions, and taking care to tighten the peripheral bolts in a symmetrical manner during assembly, leakage could be eliminated even when membranes of a nonspongy character were used. The surfaces had, however, to be kept scrupulously clean when the instrument was dismantled.

The valve blocks were also of bronze, with needle values of stainless steel. Using these two metals, finger-tight pressures were quite sufficient to ensure a completely liquid-tight seal at the valve seatings. At no time over a period of three years has leakage from this source ever arisen.

The capillaries were 1 mm. in diameter and were cut from adjacent parts of the same tube. The glass-metal seals used in construction were of Pyrex and copper, the capillary being attached close to the seal itself. The seals were tested with an air pressure of several atmospheres before being used.

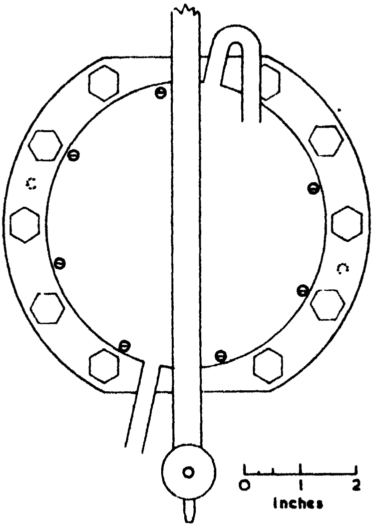

Fig. 1. Osmometer; showing position of water-jacket.

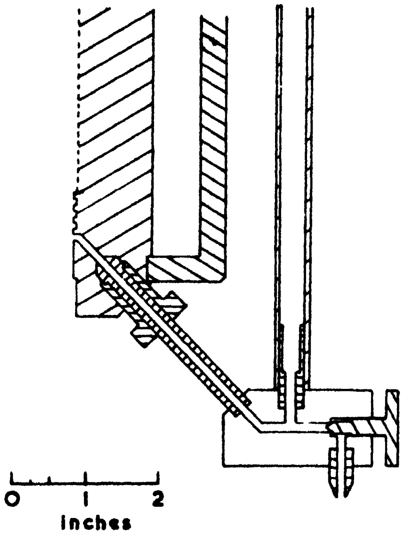

Fig. 2. Osmometer; showing position of water-jacket and lower connecting tube.

The main alterations in design were associated with the arrangements for thermostating. This was effected by means of water jackets affixed to the bronze blocks. The jackets were machined from solid bronze, and were fixed to the outer faces of the blocks by means of long screws passing through the outer rim, which was 0.35 in. thick. The contact between the rim of the water jacket and the face of the block was made tight by a paper washer. As shown in Figure 1, the water jackets did not entirely cover the block faces, since it was necessary to leave a small area of the latter free to allow manipulation of the hexagonal bolts holding the blocks together. The inner diameter of the water jackets was 4.3 in., which is slightly greater than the inner diameter of the osmotic cells (4 in.).

In order that as large an area as possible of the block faces might be covered by the water jackets, the position of the tubes connecting the valve blocks to the foot of each cell had to be altered. These tubes were made to pass obliquely through the lower edge of each block, as shown in Figure 2, instead of horizontally through the block faces as in the original instrument. This arrangement had the further advantage of ensuring more effective draining of the cell contents, since the tubes sloped continually downward from their point of entry into the two half-cells.

The instrument was made symmetrical by making provision for two stem valves instead of one, enabling the contents of either cell to be sealed off from the liquid in the corresponding stand-tube. The main advantage offered here is in enabling leakage to be tested in a much more sensitive manner than in the previous instrument. With both valve stems inserted, any drop which occurs in the capillary levels on standing must be due entirely to leakage (due allowance being made for evaporation from the capillaries). In the original instrument, however, with only one stem valve available, it is difficult to isolate effects due to leakage from those due to evaporation of solvent from the solution stand-pipe.

The two stand-pipes in the present instrument were constructed of brass, eliminating two glass-metal seals in the original. All borings were 1/8 in. in diameter to permit rapid filling and washing of the cells when working with viscous solutions. The size of the needle valves was correspondingly altered.

This osmometer, which is manipulated in the same manner as the Fuoss-Mead instrument, retains all the advantages of the original, while the modifications introduced have considerably increased its scope and usefulness for molecular weight measurements. In particular, the thermostating arrangements have enabled measurements to be performed on low-molecular polymers where the use of relatively slow membranes is necessary. Such measurements could not be carried out using the straight design of Fuoss and Mead.

THE THERMOSTAT AND WATER CIRCULATION

The good performance of the thermostated osmometer was due largely to accurate temperature control of the water reservoir and rapid passage of water through the instrument by an efficient circulating pump. The control system for regulating the bath temperature consisted of a valve circuit operated using a B.V.A. type GT 1C thyratron relay and mercury-toluene regulator. Two heating bulbs were employed, each consisting of an 120-watt lamp. The main heating lamp was in series with an adjustable rheostat and served as a variable source of heat by means of which the bath could be maintained to within one or two degrees of the desired temperature. The regulating lamp in the anode circuit of the valve dissipated only 60 watts, since only alternate mains half-cycles are passed by the thyratron.

All water leads were as short as possible. The central, thermostated part of the osmometer was shielded from draughts by a wooden box through which the capillaries projected. The presence of this box was necessary to keep the temperature drop between the bath and the osmometer at a minimum. The box had occasionally to be packed with cotton waste.

With rapid stirring of the water in the tank it was possible to keep the temperature in the bath constant to ±0.01°C. after temperature equilibrium with the osmometer had been established. In view of the large heat capacity of the cell blocks, it is believed that the temperature of the osmometer does not vary to a much greater extent than that of the bath provided the experiments are performed in the regions of room temperature. This is supported by the observation that, unless working at elevated temperatures or with membranes of extremely low permeability, the movements in the meniscus level after osmotic equilibrium had taken place could always be kept within the limits of experimental observation (±0.01 cm.).

CORRECTION FOR EXPOSED CAPILLARIES

Using this type of osmometer, osmotic pressures are measured in centimeters of solution. For the calculation of results it is not necessary to measure the density of the solution provided the concentration is determined by weight (grams per 100 g. solution). Using these units the density of the solution drops out of the expression for π/c so that this value is the same as that obtained when π is expressed in centimeters of water and c in grams per 100 cc. of solution.

However, the density of the solution cancels out in this way only if the temperature of the solution is the same in the capillary and the osmotic cell. This is the case in the original, nonthermostated instrument, but in the modified osmometer the capillaries are at room temperature while the cells are at approximately the temperature of the bath. (Actually, there will be a temperature gradient along the capillaries, but in the region of the osmotic head the mean temperature may be regarded as being very nearly equal to room temperature.)

The error involved in neglecting this density difference between the solution in the osmotic cell and in the capillary is small, but may be without experimental error. If the temperature difference between the osmometer and the laboratory exceeds about 10°C., it is generally necessary to apply a correction to the value of π/c. The value of π/c calculated from the measured quantities is multiplied by a factor

$$(d^{t_1^\circ}/d^{t_2^\circ})$$

where $d^{t_1^\circ}$ and $d^{t_2^\circ}$ are the densities of the solution at room temperature and at the temperature of the osmometer, respectively. Since the correction term involves only the ratio of the two densities, it is sufficiently accurate in dilute solution to use the densities of pure solvent at the two temperatures instead of the densities of the solution, so that:

$$(\pi/c)_{\text{corrected}} = (\pi/c)_{\text{calculated}} \times (d^{t_1^\circ}/d^{t_2^\circ})_{\text{solvent}}$$

The correction term does not generally affect the value of π/c by more than 0.03 units. It does not decrease appreciably with increasing dilution, but since the experimental error in π/c becomes greater in dilute solution, the correction can usually be ignored at concentrations less than about 0.5%. In cases in which it has been applied to the results, the solvent densities were measured over a range of temperatures by means of an Ostwald-Sprengel pycnometer, and the required values obtained graphically.

MEMBRANES

Two factors govern the choice of a semi-permeable membrane for osmotic work: (a) permeability to solute, and (b) permeability to solvent. These factors may not be independent of one another, and both govern the accuracy of the results. Strict impermeability to the smallest solute molecules is the first condition of the membrane. For this condition to be satisfied, however, it may be necessary to use a membrane which shows only a low permeability to the solvent, and the measurements become very time consuming. This is particularly true of measurements on low-molecular polymers or on unfractionated polymers containing the low-molecular species. With polymers from which the smallest molecular fractions have been removed, the difficulty is not so great, and faster membranes can be used. It is here that the dynamic method of measurement described by Fuoss and Mead (1) has proved most successful. It is obviously desirable to be able to extend this method to cases in which the solute molecules are small, but there is a real lack of suitable membranes for the purpose. The type of membrane described below overcomes this difficulty to a large extent.

Bacterial Cellulose as Membrane

Preparation of the Cellulose

Bacterial cellulose is a natural variety of cellulose obtained by the growth, under suitable conditions, of Acetobacter xylinum in a medium containing alcohol and a hexose sugar (or some compound giving rise to a hexose under the experimental conditions). The method of preparation has been described by various authors (2). The product, after thorough washing for a prolonged period, is cellulose of a very pure character. The structure of the material has been examined by Franz and Schiebold (3), Sisson (4), and by Frey-Wyssling and Mühlethaler (5). A preliminary account of its use as a material suitable for osmometer membranes has been given (6).

For the bacteriological preparation of the membranes used in this work, the authors are indebted to Professor J. Cruickshank and Dr. R. F Menzies of the Bacteriology Department of this University. The method employed was that described by Aschner (2c). Membranes of size convenient for use in the osmometer were grown in circular vessels approximately 6 in. in diameter. The vessel was covered with a glass plate which was slightly tilted to allow free access of oxygen. Any condensed moisture was thus drained to the edge of the dish. (When a watch glass is used as cover, condensed moisture drops back into the vessel and retards growth at the center of the membrane.)

The bacterium (Acetobacter xylinum, N.C.T.C. 1375) is grown at 30°C. in a sterilized medium of yeast extract, acetic acid, sucrose, and alcohol. In order to obtain a membrane of uniform thickness, the irregular film which eventually appears after 24 hours on the surface of the medium is removed with aseptic precautions and discarded. Withdrawal of this film also removes most of the fine particulate matter suspended in the medium. Incubation is then allowed to proceed until a membrane 4-5 mm. in thickness is obtained. Starting with a fresh culture of bacteria, membranes of this thickness are obtained in about 4 days after removal of the first film. Such membranes are free from contaminating particles and are quite uniform in thickness.

At this stage the membrane is removed, rinsed in water, and treated with 5% caustic soda at 37°C. for 24 hours to dissolve the incorporated bacteria. It is finally washed for 24 hours in running water to remove the dissolved bacteria and excess caustic. The membranes in this state are translucent in appearance and very spongy in character due to the large amount of water which they contain. Hibbert and Barsha (2a) report that such membranes contain water to the extent of about 10,000% of their dry weight.

Control of Permeability

In this highly swollen state, the membranes are unsatisfactory for use in the osmometer on account of their high permeability to polymer molecules in solution. In experiments with the highly swollen material, the membranes were soaked for 24 hours in several changes of alcohol to displace the water. They were then treated with successive changes of benzene for about an hour. On transference to benzene the membranes lose their opaqueness and become quite transparent, but milky patches on the membranes sometimes resulted if complete removal of the water had not been effected. The membranes were therefore allowed to stand for a half-hour in absolute alcohol before transference to the solvent in order to ensure complete removal of the last traces of water.

Using a highly swollen membrane in the osmometer, several seconds were sufficient for equilibrium to be established with benzene in both half-cells. With a 2% solution of polyvinyl acetate of molecular weight 100,000 in the solution half-cell, no osmotic pressure was established, and after standing for an hour, almost 2% of the solute diffused through the membrane.

To reduce the permeability of the membranes, use is made of the property of bacterial cellulose, that, once dried out, it reswells to only a very limited extent of its original thickness. Depending on the nature of the drying process, the structure of the cellulose is altered in this treatment (4a), and for strict semi-permeability of the membranes, the actual manner of drying is important. Unless the membranes are allowed to dry in contact with a smooth surface or under stress, they invariably become wrinkled in nature. The presence of such wrinkles leads to solute diffusion when the membrane is later placed in the osmometer. Two suitable methods of obtaining wrinkle-free membranes are as follows. In both methods the bulk of the water is first removed from the highly swollen membrane by mechanical pressure, the membrane being placed between filter papers. (1) The partially dried membrane is placed on a film of liquid paraffin in a Petri dish and left to dry in an oven at 100°C. When dry, the membrane is freed from liquid paraffin by washing in benzene. (2) The membrane is spread on a plate of highly polished stainless steel, covered with a filter paper and squeegeed on the plate. The wet filter paper is removed and the process repeated till almost all the water has been forced out. The membrane is then lightly covered with a filter paper and left overnight to dry out completely at room temperature. On drying, the membrane usually comes off the polished surface by itself, but it may adhere to the surface in some parts even when quite dry. If this occurs, the membrane must be rewetted, replaced lightly on the plate, and again left to dry. This second drying takes place much more rapidly then the first, and the membrane removes itself completely from the plate in a few hours. The latter method of drying is preferred since it avoids contamination with any low-molecular foreign substance. Once the membrane has been dried out, care is necessary in all subsequent handling to prevent wrinkling of the surface.

Membranes dried in the above manner are completely impermeable to organic solvents like benzene and absolute alcohol. They are brought to the desired permeability by reswelling in water or alcohol-water mixtures. For membranes which have been dried out and reswollen, conditioning to the solvent is accomplished in a much shorter time than for the highly swollen cellulose. The sequence of operations shown in Table I is sufficient for conditioning.

TABLE I. Sequence of Operations for Conditioning the Membranes

Organic liquid	Number of washings	Total time, hours
Alcohol	5	2
Absolute alcohol.	1	1/2
Solvent	4	1

Following Carter and Record (7) for Cellophane, a membrane designated as x/(100 - x) is one which has been reswollen in x cc. alcohol and (100 - x) cc. water. The acutal degree of swelling required to give the most permeable membrane which may be used for a particular polymer-solvent system must be determined by experiment. As a guide, Table II shows the degree of swelling successfully em-

TABLE II. Degree of Swelling of Membranes Required for Various Systems

Polymer	Solvent	Molecular weight of polymer	Ratio: alcohol/water
Polymethyl methacrylate	Benzene	Over 700,000	0/100
Polymethyl methacrylate	Benzene	Over 40,000	60/40
Polyvinyl acetate	Benzene	90,000-200,000	50/50
Polyvinyl-xylene	Benzene	260,000-440,000	0/100
Polyacrylonitrile	Dimethyl-formamide	33,500	50/50
Polyethylene sebacate	Chloroform	11,400	90/10*

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*Indicates that a static method must be employed.

ployed in measuring molecular weights of the order of magnitude indicated. The polymers referred to are all heterogeneous samples.

No solute permeation could be detected in any of these systems using the appropriate membrane for each. A (0/100) membrane proved too permeable for the polyvinyl acetate samples even when the molecular weight was as high as 200,000, and a (50/50) membrane had to be employed. For fractionated samples of this polymer, however, a (0/100) membrane was used with success down to a molecular weight of 129,000.

In cases where solute permeation of the membrane occurs it can be detected in the following various ways.

(a) A downward drift in the osmotic pressure is observed on standing. (Using a low-molecular gelva (Gelva 7) in conjunction with a (0/100) membrane, a negative osmotic pressure was actually produced in a short time.)

(b) Asymmetric Fuoss-Mead rate curves leading to a decreasing equilibrium value was obtained.

(c) A turbidity is produced on pouring the contents of the solvent cell into nonsolvent at the end of an experiment.

(d) A negative "cell constant" is produced.

Typical Rate Curves

For membranes which have been fully reswollen in water, Fuoss-Mead rate curves of the type shown in Figure 3 are obtained, where Δh, the difference in centimeters between the meniscus levels, is plotted against time, in minutes. Here, osmotic pressures may be determined in less than an hour after filling the cells. For 50/50 membranes, the time required for complete run is $1\,^1/_2$-2 hours. A typical rate curve for such membranes is shown in Figure 4. In this case, unless the value of the osmotic head is known with a fair degree of certainty before the run is commenced, it is necessary to take read-

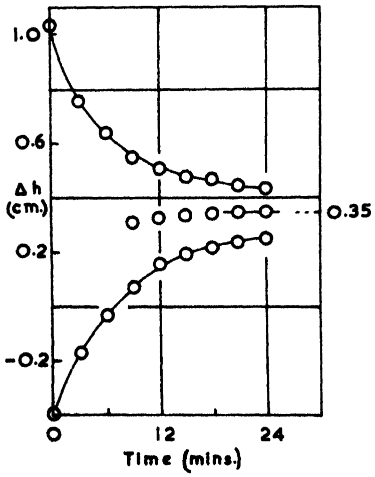

Fig. 3. Fuoss-Mead rate curves for bacterial cellulose, dried and reswollen in water. (Polyvinylxylene, 0.285% in benzene.)

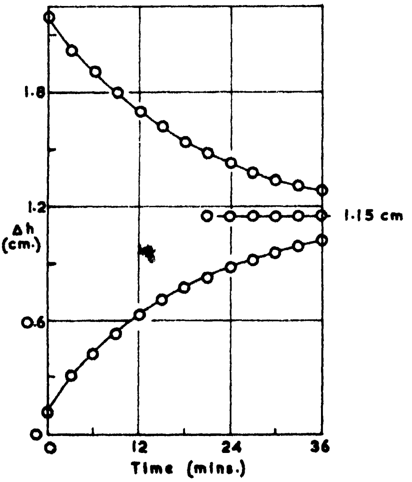

Fig. 4. Rate curves for bacterial cellulose, dried and reswollen in 50/50 alcohol-water. (Polyvinyl acetate, 0.404% in benzene.)

ings over a somewhat longer period than that indicated by the plot. The curves obtained are then "matched" by displacement on the time axis until the true position for symmetry is obtained.

For other degrees of swelling, the curves are similar, but the dynamic method ceases to be of practical use when membranes of permeability less than about (80/20) are employed. Such membranes must be used when dealing with polymers having molecular weights less than about 20,000. In these cases, the time required for measurements is so long that a static method of determination, although probably less accurate, is more convenient.

An unusual feature of the membranes is that their permeability decreases with increasing concentration of the solutions. Figure 4 represents the rate curves for a solution of polyvinyl acetate (molecular weight 115,000) of concentration 0.404 g./100 g. in benzene (50/50 membrane). The rate curves obtained for a more concentrated solution (1.049 g./100 g.) of this polymer, using the same membrane, are shown in Figure 5. In this case, a considerably longer time would be necessary for the full development of the pressure head. The effect, which has been noted also for Cellophane membranes by Robertson, McIntosh, and Grummitt (8), was not studied quantitatively, since absolute permeabilities cannot be conveniently measured using the Fuoss-Mead type of osmometer. The behavior does not appear to be due to the passage of small solute molecules through the membranes, and was a general feature of all the experiments.

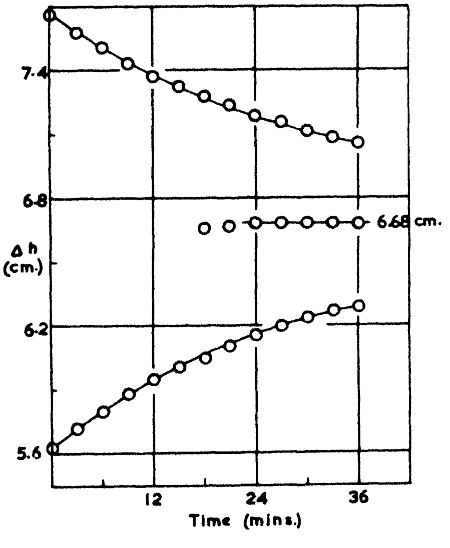

Fig. 5. Rate curves for polyvinyl acetate, 1.573% in benzene; 50/50 membrane.

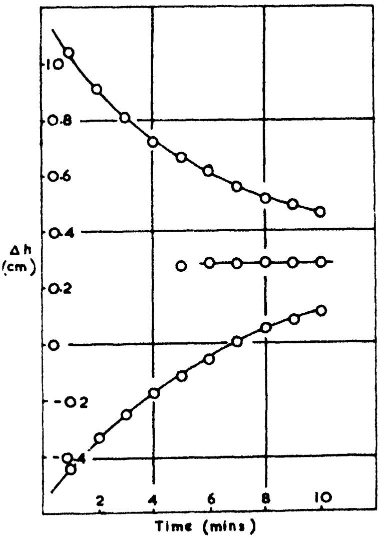

Fig. 6. Rate curves for bacterial cellulose, approximately 2 mm. initial thickness, dried and reswollen in water. (Polymethyl methacrylate, 0.700% in benzene.)

Other Factors Affecting Membrane Permeability

Apart from the degree of swelling and the above effect associated with the concentration of the solutions, various other factors affect the permeability of bacterial cellulose membranes.

Age of the Culture

Membranes which have been harvested from old cultures are considerably less permeable than those obtained using a young culture of bacteria for each preparation. In cases where the culture medium is almost exhausted, a considerably longer time than four days may be necessary for growth to the desired thickness. Such membranes are generally so dense as to be unsuitable for use as "dynamic" membranes even on reswelling to their maximum extent in water. For reproducibility of results it was necessary to use membranes prepared from a young culture of bacteria each time.

Effect of Thickness

4-5 mm. (in the highly swollen state) is regarded as being the most suitable thickness of membrane for osmotic work. Membranes thinner than this often showed permeability to the solute molecules, although membranes of approximately 2 mm. swollen thickness have been used with success for high-molecular polymethyl methacrylates (molecular weight greater than 700,000). A typical rate curve for such a membrane, fully reswollen in water, is given in Figure 6. Here, only ten minutes are required for each half-run.

Results obtained using membranes of initial thickness greater than 5 mm. were not reproducible. This is believed to be due to uneven bacterial growth beyond this stage consequent upon an insufficency of oxygen penetrating through the membrane to the bacteria. For reproducible permeabilities, the technique of limited swelling using membranes up to 5 mm. in thickness is regarded as being the most satisfactory procedure.

Aging of Membranes

In common with Cellophane, bacterial cellulose slowly loses its permeability on prolonged standing in certain solvents, most notable being benzene and absolute alcohol. Membranes were therefore stored in the dry state and reswollen as desired. The effect appears to be structural collapse toward some limiting measure of porosity, since it is most marked in the case of membranes which have been reswollen to their maximum extent. Scarcely any change in permeability, for example, could be detected over a period of about a year for a 60/40 membrane stored in benzene in the osmometer.

The Cell Constant and Other Phenomena

The Cell Constant

When new, bacterial cellulose membranes do not exhibit any asymmetry in the form of a cell constant, provided the osmometer is quite free of leaks. After the membranes have been used for some time, however, and in particular if they have been allowed to stand overnight in contact with solution, a small but definite value is obtained. Once developed, the cell constant rarely disappears, even after the membrane has been standing for about two months in contact with pure solvent. On such prolonged standing, however, the value usually decreases.

The value also decreases to a minimum on washing the membrane repeatedly with solvent. Experiments have shown that the value becomes appreciably constant after about six rinsings. Before measuring the value of the cell constant, the standard procedure adopted was to rinse the membrane six times on each side with pure solvent, fresh solvent being used for each washing. In work demanding the highest accuracy (i.e., when working with very dilute solutions or when dealing with polymers of molecular weight higher than about 500,000) the cell constant was measured after each osmotic pressure determination and this value taken as the true value to be applied as correction.

When working repeatedly with the same type of polymer, the value of the cell constant usually settled to some definite amount for a particular membrane, and only an occasional run was necessary to check this. The value was generally positive, i.e., in the same sense as the osmotic pressure; negative values were encountered only after solute diffusion through the membrane was observed to have taken place. Negative cell constants could thus be regarded as a warning that the membrane was too permeable for the particular polymer in use.

These observations would indicate that the cause of the cell constant is slight adsorption of polymer molecules on the surface of the membrane. Such adsorption has been reported also for Cellophane membranes (8). Unsuccessful attempts were made to eliminate the cell constant by placing the solutions alternately on either side of the membrane during a series of measurements, and the most accurate procedure seemed to be direct measurement and application of the ncessary correction.

Membrane Blockage

It was occasionally the case that a new membrane which allowed solute diffusion to occur to only a slight extent could be made impermeable to the solute by allowing it to stand in contact with the solution for a few days. This effect has been termed, after Hoff (9), "membrane blockage." Even after thorough washing with pure solvent or after standing for several days under a head of solvent, such membranes still retained their impermeability to solute, and could be used as truly semi-permeable membranes. The phenomenon, however, did not occur with all polymers, a notable exception being polyvinyl acetate, for which the membranes had always to be strictly semipermeable from the start before reliable results could be obtained.

Adsorption Effects

In carrying out osmotic pressure measurements, low values were often obtained if the membrane had not been rinsed sufficiently on the solution side prior to a determination. This effect has been noted for both Cellophane (8) and denitrated collodion (1) membranes. McIntosh et al. (8) attribute the cause to adsorption of polymer on the Cellophane membrane. In the case of bacterial cellulose the effect is not so pronounced, and nothing in the nature of the "time lags" reported for Cellophane have ever been observed. The osmotic pressure values obtained for a stock solution of Commercial Gelva 60 in benzene on the first four fillings are given in Table III. (Concentration of solution, 0.821 g./100 g.)

Here the osmotic pressure values become constant after the third filling. In carrying out measurements the technique adopted in all cases was to rinse the membrane six times on the solution side prior to a determination. The solvent cell was rinsed simultaneously, fresh solvent being added at the final filling.

TABLE III. Effect of Repeated Rinsing of Membrane with Polymer Solution (50/50 Membrane)

Filling	π, cm. solution		π/c
1	1.84		2.24
2	1.93		2.34
3	1.98	1.98	2.41
4	1.97		

DISCUSSION

The usefulness of bacterial cellulose as a material for osmometer membranes lies in the fact that its permeability may be controlled over a wide range of values. Control of the permeability may be effected either during growth of the cellulose itself or during subsequent treatment. This enables individual membranes to be prepared for use with particular polymers so that the maximum speed compatiable with strict semi-permeability may be achieved in each case. In particular, measurements on heterogeneous polymer samples containing low-molecular material may be carried out in a reasonably short time using a dynamic method, where otherwise a lengthy static method would probably have been necessary.

In addition, such membranes are not subject to the same uncertainties involved, for example, in the use of Cellophane. Adsorption effects are small, and reproducible results are obtained merely by washing the solution cell thoroughly before measurements.

The membranes may be used for measurements on polymers having molecular weights as low as 10,000, but here a static method is necessary. It is in this relatively low-molecular region that new techniques for measuring molecular weights rapidly and reliably are now most urgently required. Such measurements would yield useful information concerning the thermodynamic behavior of systems in which the solute molecules lie intermediate in size between "ordinary" dimensions and the dimensions of macromolecules.

Acknowledgment

We should like to thank the Distillers Company Ltd. for the award of a Postgraduate Scholarship to one of us (C.R.M) which made it possible to carry out these researches.

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Synopsis

The construction of a thermostated osmometer of the Fuoss-Mead pattern is described. The technique of preparation of bacterial cellulose membranes for osmotic measurements on high polymer systems is given. The permeability of such membranes may be controlled by growth to a thickness of 4-5 mm., drying in contact with a stainless steel surface, and reswelling in water or alcohol-water mixtures. The degree of reswelling required to give membranes suitable for use with polymers of a range of molecular weights is given. The factors affecting the behaviour of the membranes in the osmometer are discussed.

Résumé

La construction d'un osmomêtre thermostatisé du type Fuoss et Mead est décrite. Les auteurs indiquent également le mode de préparation de membranes cellulosiques bactériennes pour des mesures osmotiques applicables aux hauts polymères. La perméabilité de ces membranes peut être controlée par gonflement de celles-ci jusqu'à une épaisseur de 4-5 mm., en les séchant au contact d'une surface en acier inoxydable, et en les regonflant dans l'eau ou dans des mélanges alcool-eau. Les auteurs indiquent le degré de regonflement, nécessaire à l'obtention de membranes utilisables pour des polymères présentant un poids moléculaire déterminé. Les facteurs, qui influencent le comportement de la membrane dans l'osmomêtre, sont discutés.

Zusammenfassung

Die Konstruktion eines Fuoss-Mead schen thermostatischen Osmometers wird beschrieben. Die Art der Herstellung bakterieller Cellulosemembranen für Messungen des osmotischen Druckes polymerer Systeme wird erläutert. Die Durchlässigkeit solcher Membranen kann dadurch festgestellt werden, dass man sie bis zu einer Dicke von 4-5 mm wachsen lässt, sie dann an einer Nickelstahlfläche trocknen lässt- und sie in Wasser oder Wasser-Alkohol-Mischungen neu aufquellt. Das Ausmass des Quellens, das für Membranen notwendig

ist, die für Polymere verschiedener Molekulargewichte verwendet werden sollen, ist gegeben. Die Faktoren, die auf das Verhalten der osmotischen Membranen beeinflussen, werden erörtert.

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Osmometry of High Polymer Solutions. II. Osmotic Measurements Using Bacterial Cellulose Membranes

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In a previous communication (1) the technique of preparation of bacterial cellulose membranes has been described, and the factors affecting membrane behavior have been discussed. Membranes of this character have been used in the dynamic osmometer of Fuoss and Mead (2) and in the modified instrument previously described (1) to measure the molecular weights of a number of high polymers. These measurements are described below.

EXPERIMENTAL PROCEDURE

Membranes

The membranes used in this work had (with one exception) an initial thickness of 4-5 mm. in the highly swollen state. Their permeability was controlled by drying and reswelling in water or alcohol-water mixtures. For the fastest membranes (i.e., membranes reswollen in water alone), the original Fuoss-Mead osmometer could be used for the measurements; otherwise the thermostated instrument had to be employed.

Solutions

Both Commercial and laboratory prepared polymer samples were employed. Initial solutions were prepared by overnight tumbling. When necessary, these solutions were filtered through sintered glass till they appeared clear in the beam of a carbon arc. Subsequent solutions were prepared by dilution.

Measurement of Osmotic Pressures

Measurements of the meniscus levels were made using a cathetometer, readings being taken to the nearest hundredth of a centimeter. The standard procedure adopted in measuring all osmotic pressures was as follows. The half-cells were rinsed six times with solution and solvent prior to each run. The osmotic pressure was then determined either dynamically or, where necessary, statically. At the end of the run a small portion of the solution was run off for determination of the concentration. The osmometer was drained, rinsed six times on both sides with solvent, and the cell constant determined either dynamically or by standing overnight. The cells were

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rinsed with solvent between measurements even when the cell constant was not to be determined. In such cases, the value of the cell constant was estimated from other values measured during the same series of experiments.

Measurements of Concentrations

Concentrations were initially determined by evaporating a portion of each solution to constant weight at 100°C. in an oven through which a stream of preheated air could be drawn. In converting to units of grams per 100 cc., the density of the solution was taken to be equal to that of pure solvent in the low concentration range studied.

The work of Grassie and Melville (3) on polymer degradation, however, has shown that this method of determining concentrations is inaccurate, since the film of polymer that is formed on the walls of the containing vessel may still retain an appreciable percentage of volatile material. To drive off these volatiles it is necessary to heat the polymer film in vacuo to a temperature above the softening point. For this purpose, a modified form of the molecular still designed by Grassie and Melville has been constructed. By means of this apparatus (constructional details to be given shortly in a separate communication) the weighing bottle containing the polymer film may be heated in vacuo to the desired temperature and the percentage of volatiles remaining in the film after the first treatment may be estimated.

For polymethyl methacrylate in benzene, the percentage of volatiles removed from the film by this treatment is 6.3%, and all values of c and π/c shown in the results for this system have been correspondingly corrected. For polyvinyl acetate in benzene and ethyl acetate, the loss in weight of the film is negligible (only 0.3%); this may be attributed to the fact that the softening point of this polymer is well below 100°C., so that almost all the volatiles may be driven off by prolonged heating at this temperature. The concentration values quoted for this polymer may therefore be regarded as being accurate to 0.3%, so that no correction need be applied to the results for π/c. In the case of polyacenaphthylene in benzene, when the solvent is evaporated off at 100°C. the bulk of the polymer is deposited in crystalline form instead of forming a film on the walls of the vessel. Heating to 260°C. in vacuo resulted in the crystals losing 1.5% of their weight, and further heating at this temperature did not cause any further decrease in weight. All values of c and π/c were therefore corrected by this amount.

For the other two systems studied, the concentration values are uncorrected, so that the values of π/c must be regarded as being several per cent too low and the molecular weights correspondingly too high. Since the measurements cover a very limited concentration range, the slopes of the π/c - c curves will not be greatly altered, and the Huggins μ values should not be in error by more than 0.01.

EXPERIMENTAL RESULTS

Polyvinyl Acetate in Benzene

Polymers. Five polymer samples were investigated. Three were Commercial Gelvas obtained from Shawinigan Ltd. and designated Gelva 25, 45, and 60 in order of increasing molecular weight as indicated by viscosity measurements. The other two samples, designated 1221 and 2410, had been prepared in these laboratories by G. M. Burnett by photopolymerization of the liquid monomer in vacuo. The kinetic coefficients for this reaction have been measured by Burnett and Melville (4), so that the chain lengths of the samples were known with certainty. The chain lengths are given by the ratio (over-all rate)/(rate of starting), both of which quantities may be measured directly by experiment. For the first sample the rate of initiation was 1.27×10^{-8} einstein liter^{-1} sec.$^{-1}$ and the measured over-all rate was 1.55×10^{-5} mole liter^{-1} sec.$^{-1}$. Hence:

$$\nu_n = 1221 \quad \text{or} \quad M = 105{,}000$$

ν_n being the chain length and M the molecular weight. Similarly the second sample had:

$$\nu_n = 2410 \quad \text{or} \quad M = 208{,}000$$

This method of computation assumes that any transfer reaction is of negligible importance. Had transfer occurred, the expression for ν_n would become:

$$1/\nu_n = k_f/k_p + (k_t^{1/2}\, I^{1/2})/(k_p(M))$$

where k_p, k_f, and k_t are the velocity coefficients for propagation, transfer, and termination, respectively; I is the rate of chain initiation and (M) the stationary monomer concentration. Comparison with the corresponding expression for ν_n assuming no transfer:

$$1/\nu_n = (k_t^{1/2}\, I^{1/2})/(k_p(M))$$

shows that any transfer reaction, if appreciable, would lead to smaller molecular weight values than those quoted above.

Membranes. (50/50) membranes had to be employed for all the polymers in order to avoid solute permeation. The same membrane was not used throughout, and the time required for a half-run varied between 35 and 50 minutes depending on the particular membrane in use.

Results. The complete results for all polymers are given in Table I. The temperature of measurements was 20°C. for the laboratory samples and 20.4°C. for the Gelvas. The cell constant values given in parentheses are estimated from the measured values. P is the observed pressure head and π the osmotic pressure, both in centimeters solution. The values of π/c refer to π in centimeters water and c in grams per 100 cc. solution.

In Figure 1, π/c is plotted against c for all five polymers. The relationships are best represented by a series of curved lines corresponding to an equation:

$$\pi/c = A + 1.35\, c^{1.27}$$

and all curves have been extrapolated on this basis. The extrapolated values of $(\pi/c)_0$ and the corresponding values of M are listed in Table II. The estimated error in M assumes an uncertainty of 0.09 units in $(\pi/c)_0$.

Figure 2 shows the plot of $\pi/c - RTd_1c^2/3M_1d_2^3$ against c for polymer 1221, as recommended by Huggins (5) for systems which exhibit a curved π/c - c relationship. The curvature is not completely accounted for by this expression, so that the value of the Huggins constant μ would appear to be concentration-dependent over the range shown. The values calculated for μ are 0.44 at $c = 0$, and 0.41 at $c = 1.2\%$. It is of interest to note that the values of $(\pi/c)_0$ for polymers 1221 and 2410 calculated on the basis of the kinetic chain lengths are 2.37 and 1.20, respectively. The osmotic results could not be interpreted to yield values of $(\pi/c)_0$ larger than these quantities, so that the absence, or at least the negligible importance of transfer in the polymerization reaction, is demonstrated conclusively. Transfer being absent, the kinetic values of M must be regarded as being fairly precise, so that the curvature displayed by the π/c - c plots would seem to be real.

TABLE I. Osmotic Measurements for a Series of Polyvinyl Acetates in Benzene

Polymer	Concentration, g./100 cc.	p	Cell constant	π	π/c
1221	1.382	6.68	0.17	6.51	4.14
	0.923	3.59	0.15	3.44	3.28
	0.689	2.45	(0.14)	2.31	2.94
	0.597	2.05	0.14	1.91	2.81
	0.355	1.15	0.13	1.02	2.51
2410	1.041	3.16	0.11	3.05	2.58
	0.678	1.73	0.14	1.59	2.06
	0.459	1.02	0.11	0.91	1.74
G. 25	0.899	4.23	0.21	4.02	3.93
	0.570	2.59	(0.19)	2.40	3.46
	0.328	1.30	0.16	1.14	3.05
G. 45	1.435	6.81	0.36	6.45	3.95
	0.888	3.34	(0.32)	3.02	2.99
	0.647	2.14	(0.28)	1.86	2.52
	0.459	1.51	0.24	1.27	2.44
G. 60	0.993	3.13	0.17	2.96	2.62
	0.722	1.98	(0.16)	1.82	2.22
	0.529	1.38	0.15	1.23	2.04

TABLE II. Molecular Weights of Polyvinyl Acetates

Polymer	$(\pi/c)_0$	$M \times 10^{-4}$	Estimated error in M
1221	2.06	12.1	± 5,000
2410	1.17	21.2	±14,000
G. 25	2.73	9.1	± 3,000
G. 45	1.77	14.1	± 6,000
G. 60	1.30	19.1	±12,000

The above values of μ agree well with the value of 0.428 found by Sirianni, Wise and McIntosh (6) over a concentration range of 0.8 to 1.2%. The molecular weight found for Gelva 45 is also in good agreement with the value of 147,000 found by Robertson, McIntosh, and Grummitt (7) using caustic-treated Cellophane as membrane.

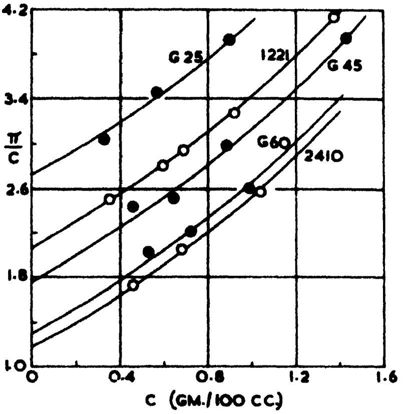

Fig. 1. π/c - c relationships for polyvinyl acetate in benzene: ●, Commercial Gelvas; 0, polymers of Burnett and Melville.

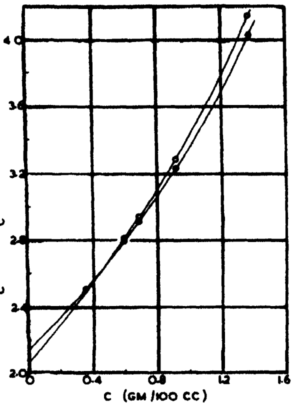

Fig. 2. Effect of the term $RTd_1c^2/3M_1d_2^3$ on the results for polyvinyl acetate in benzene: 0, π/c vs. c; ●, $\pi/c - RTd_1c^2/3M_1d_2^3$ vs. c.

Polyvinyl Acetate in Ethyl Acetate

The osmotic results for Gelva 45 in ethyl acetate as solvent, using a (50/50) membrane, are given in Table III. Figure 3 shows the π /c - c plot for this system along with the corresponding curve for benzene. In this case the plot is linear, the system having a μ value of 0.415.

TABLE III. Osmotic Results for Gelva 45 in Ethyl Acetate

c, g./100 cc.	P	Cell constant	π	π/c
1.254	5.56	0.12	5.44	3.89
0.898	3.47	0.14	3.33	3.34
0.618	2.02	0.05	1.97	2.86
0.432	1.32	0.10	1.22	2.54

Polymethyl Methacrylate in Benzene

Polymers. Four samples of polymer were used. One of these, designated A 356, was a commercial, unplasticized "Perspex," obtained from I.C.I. Ltd. The other three samples, labelled P.M.1, P.M.2, and P.M.3, had been prepared in these laboratories by W. F. Watson by thermal polymerization of the monomer using benzoyl peroxide as catalyst, and were believed to be of high molecular weight.

Membrane. The same membrane was used for all the measurements. This membrane was thinner than those normally employed, having an initial thickness of only 2-3 mm. It was reswollen in water alone. Only ten minutes were required for each half-run, and the non-thermostated Fuoss-Mead osmometer was used for the measurements at a mean temperature of 16°C.

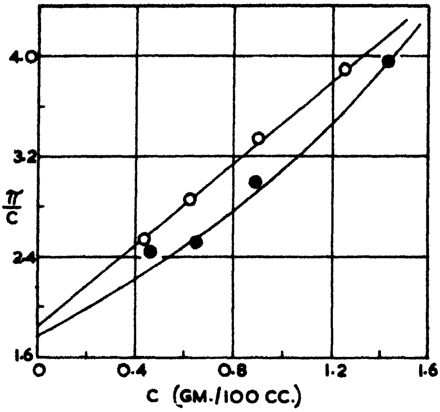

Fig. 3. π/c - c relationships for polyvinyl acetate in ethyl acetate O, and in benzene ●.

Results. A typical curve is shown in Figure 4, representing the run for the most concentrated solution of A 356. On account of the rapidity with which the rate curves become symmetrical and the freedom from temperature effects using such a fast membrane, the experimental error in π is here believed to be less than ±0.01 cm.

TABLE IV. Experimental Results for Polymethyl Methacrylate in Benzene

Polymer	c, g./100 cc.	P	Cell constant	π	π/c
A 356	0.731	0.46	0	0.46	0.56
	0.579	0.29	0	0.29	0.44
	0.535	0.25	0	0.25	0.41
	0.406	0.17	0	0.17	0.37
P.M. 1	0.656	0.52	0	0.52	0.70
	0.565	0.40	0	0.40	0.63
	0.451	0.31	0.02	0.29	0.57
P.M. 2	0.672	0.47	0	0.47	0.62
	0.574	0.36	0.01	0.35	0.54
	0.469	0.30	0.04	0.26	0.49
	0.387	0.22	0.03	0.19	0.43
P.M. 3	0.544	0.31	0.05	0.26	0.42
	0.425	0.22	0.05	0.17	0.35
	0.358	0.17	0.04	0.13	0.32

The complete results for the four polymers are shown in Table IV, and the π/c - c curves are reproduced in Figure 5. In common with Baxendale, Bywater, and Evans (8), upward curvature of the plot is found, and all curves have been extrapolated according to an equation:

$$\pi/c = A + 0.653\ c^{1.42}$$

As with the polyvinyl acetates, application of the Huggins theory to the results does not completely remove the curvature of these lines, μ varying from 0.48 at $c = 0$ to 0.46 at $c = 0.7\%$.

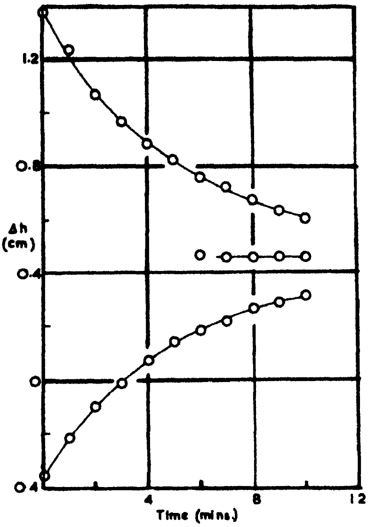

Fig. 4. Rate curves for polymethyl methacrylate in benzene using a rapid membrane.

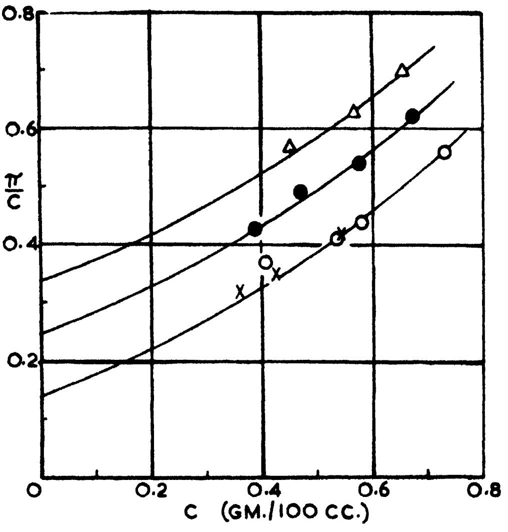

Fig. 5. π/c–c relationships for polymethyl methacrylate in benzene: Δ, P.M. 1; O, P.M. 2; x, P.M. 3; O, A 356.

Polyvinyl Xylene in Benzene

Polymers. Measurements were performed on three polymers, designated VI/106, VI/112, and VI/27. These had been prepared in the research laboratories of The Distillers Company Ltd. by thermal polymerization of the monomer in vacuo at 90°C., using tert-butyl perbenzoate as catalyst. The catalyst concentrations used were 4, 20, and 2 g./liter, respectively. Samples VI/106 and VI/112 were prepared during one set of runs; sample VI/27 was made in another set, using monomer with a slightly different history.

All samples were 100% polymerized, then precipitated twice from benzene solution by methanol and dried in vacuo at room temperature. The intrinsic viscosities in benzene at 25°C. had been measured.

Membrane. A (0/100) membrane was used throughout. This was a case in which the phenomenon of "membrane blockage" previously referred to (1) was observed. The membrane at first showed slight permeability overnight to a 0.8% solution of VI/106, a faint turbidity being produced when the contents of the solvent cell were poured into excess methanol. On adding fresh solution to the osmometer, however, no further evidence of solute permeation could be detected and the membrane could be regarded as being strictly semipermeable.

During the permeability tests, a negative cell constant developed. As shown in Table V, however, this value became less negative during the experiments.

The Dynamic Method. In attempting to measure the osmotic pressures by the dynamic method, it was observed that for the most concentrated solutions of all three polymers the rate curves were not symmetrical, so that a constant mean value for the pressure head could not be obtained. In these cases, it was necessary to determine the osmotic pressures statically. (With the fast membranes employed this did not take longer than about an hour.) The asymmetry of the curves was first thought to be associated in some way with the membrane blockage. But later measurements (notably on the system rubber-benzene) in which the membrane was strictly semi-permeable from the start, have ruled out this interpretation. Since the phenomenon may be associated with the actual mechanism by which osmotic pressures are established, the rate curves for a typical case of asymmetry are reproduced in Figure 6. These curves represent the run using the most concentrated solution of VI/112 (c = 0.684 g./100 g. solution) at a temperature of 24°C. The mean of the two curves is not constant, but shows a gradual upward drift towards the end of the run. A static value of P = 0.98 cm. solution could be obtained by approaching the equilibrium position from either side, but this value developed much more rapidly when solvent was allowed to flow through the membrane from the solution side (upper curve).

The reason for this behavior is obscure. The effect was less pronounced using more dilute solutions, and the dynamic method could be used to give a constant value for P provided sufficient time was allowed for the runs.

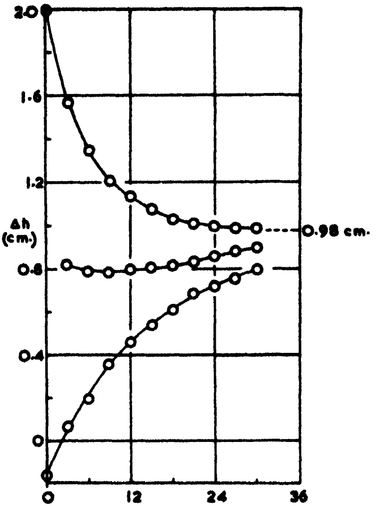

Fig. 6. Asymmetrical rate curves obtained for polyvinylxylene in benzene (polymer VI/112, concentration 0.684 g./100 gm. solution).

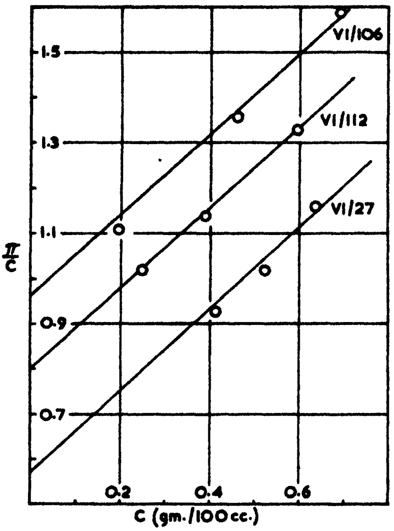

Fig. 7. π/c - c relationships for polyvinylxylenes in benzene.

Results. The complete results for the three polymers are presented in Table V, and π/c is plotted against c in Figure 7. In this case the relationship is linear and the slopes of the curves may be regarded as identical. Assuming the density of this polymer to be 1 g./cc., the slopes may be characterized by a μ value of 0.469.

In Table VI are listed the molecular weights of the three polymers and the corresponding intrinsic viscosities $[\eta]$ in benzene at

TABLE V. Results for Polyvinylxylene in Benzene

Polymer	c, g./100 cc.	p	Cell constant	π	π/c
VI/106	0.696	1.18	-0.09	1.27	1.59
	0.464	0.66	-0.06	0.72	1.36
	0.197	0.22	-0.03	0.25	1.11
VI/112	0.597	0.98	0.07	0.91	1.33
	0.392	0.58	0.07	0.51	1.14
	0.249	0.35	0.06	0.29	1.02
VI/27	0.638	0.88	0.03	0.85	1.16
	0.522	0.63	0.02	0.61	1.05
	0.414	0.44	0.00	0.44	0.93

25°C. (concentrations in base mole/liter. On account of the similar methods of preparation, the three samples may be regarded as having approximately the same degree of heterogeneity. From the limited data available, therefore, it is possible to ascribe rough values to the constants K and α in the equation (9,10):

$$[\eta] = KM^{\alpha}$$

which probably represents the intrinsic viscosity - molecular weight relationship. Plotting log $[\eta]$ against log M, as in Figure 8, the value of α obtained from the slope of the line is 0.6. Expressing concentrations in g./100 cc., a value of 5.5×10^{-4} is obtained for K.

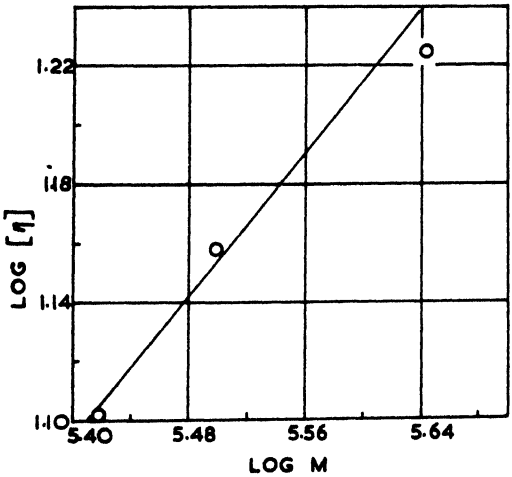

Fig. 8. Log $[\eta]$ vs. log M for unfractionated polyvinylxylenes in benzene at 25°C.

Polyacrylonitrile in Dimethylformamide

Materials and Membrane. A laboratory-prepared sample of the polymer was obtained from I.C.I. Ltd. The solvent was fractionally distilled immediately before use, the fraction boiling at 152-153°C. being collected. A (0/100) membrane was too permeable as indicated by a downward drift of the osmotic pressures on standing, and a (50/50) membrane was employed at a temperature of 13.5°C. Membrane blockage was again encountered, but after contact with a 0.6% solution for 15 hours the membrane could be used with confidence since the rate curves were perfectly symmetrical. A negative cell constant developed during the permeability tests.

TABLE VI. Molecular Weights and Intrinsic Viscosities of Polyvinylxylenes

Polymer	$(\pi/c)_0$	M	$[\eta]$
VI/106	0.96	262,000	12.65
VI/112	0.80	315,000	14.4
VI/27	0.57	440,000	16.8

Results. The results are given in Table VII. The π/c - c plot exhibits a decided curvature as shown in Figure 9. The extent of the curvature is not appreciably altered on plotting $\pi/c - RTd_1c^2/3M_1d_2^3$ against c. The value of π varies from 0.29 at c = 0 to 0.12 at c = 0.5%.

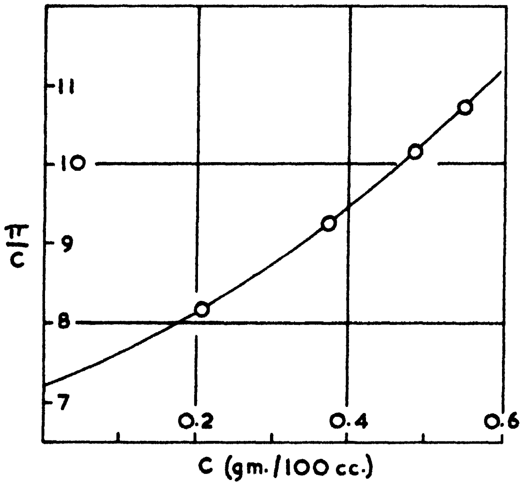

Fig. 9. π/c - c relationship for polyacrylonitrile in dimethylformamide.

The calculated molecular weight for this polymer is 33,500, the limits of accuracy being about ±1200.

TABLE VII. Results for Polyacrylonitrile in Dimethylformamide

c, g./100 cc.	P	Cell constant	π	π/c
0.550	5.72	-0.38	6.10	10.73
0.485	5.00	-0.20	5.20	10.19
0.374	3.76	+0.11	3.65	9.28
0.209	1.90	+0.10	1.80	8.19

Polyacenaphthylene in Benzene

Polymer and Membrane. The polymer sample was obtained from the Chemical Research Laboratories, Teddington. In powder form it dissolved readily in benzene yielding a clear yellow solution which was quite homogeneous. A (60/40) membrane was used after a (0/100) membrane had been found to be too permeable.

Results. Measurements were performed at 25°C. The π/c - c relationship, plotted from the results in Table VIII, is shown in Figure 10. The relationship is linear, the extrapolated value of $(\pi/c)_0$ being 2.41, corresponding to a molecular weight value of 105,000. Taking the density of the polymer to be 1 g./cc., the value of μ is 0.475.

TABLE VIII. Osmotic Results for Polyacenaphthylene in Benzene

c, g./100 cc.	P	Cell constant	π	π/c
0.888	3.61	0.51	3.10	3.04
0.721	3.16	0.75	2.41	2.92
0.549	2.50	0.74	1.76	2.80
0.360	1.84	(0.74)	1.10	2.67

Polyethylene Sebacate in Chloroform

It is of interest to know how far down the molecular weight scale bacterial cellulose membranes will remain impermeable to solute molecules while yet retaining their relatively high permeability to solvents. A check on the osmotic results at low molecular weights was provided by using a sample of polyethylene sebacate for which the number-average molecular weight had been independently determined by end-group titration. The polymer was prepared in these laboratories by G. W. Youngson and the molecular weight evaluated to be 11,000 by acetylation of the hydroxyl groups and subsequent titration with alcoholic potassium hydroxide. The end-group method of determination is not sufficiently accurate in this region to permit the molecular weight to be given to more than two significant figures, but the osmotic method gives molecular weights with an accuracy of 1%. For comparison of the results by the two methods, therefore, it is sufficiently accurate to measure only one osmotic pressure in sufficiently dilute solution and estimate the molecular weight directly without extrapolation. The π/c - c relationship was not therefore studied, and measurements were performed on a 0.065% solution by weight in water-free chloroform.

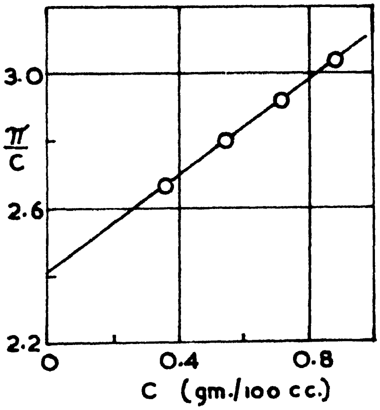

Fig.10. π/c - c relationship for polyacenaphthylene in benzene.

Experiments were first performed using a very dense specimen of the cellulose (approx. 2 cm. initial thickness), dried and reswollen in water. Such a membrane might have been expected to show a fairly high permeability toward the solvent and yet remain impermeable to the solute. However, although an osmotic pressure of about 1 cm. of solution was established in less than 15 minutes, this value decreased slowly on further standing until, after 2 hours, a small negative head (about 0.1 cm.) was obtained. The extent of the solute diffusion was measured to be 16% in 15 hours for a 3% solution of the polymer. The membrane was therefore rejected.

Next, a membrane of normal thickness (approx. 4 mm.), dried and reswollen in (70/30) alcohol/water was tried, but evidence of solute permeation was again obtained by a slow downward drift of the osmotic pressure on standing.

For complete impermeability to the solute it was necessary to resort to a membrane swollen in (90/10) alcohol/water. Using this membrane, a steady head of 1.41 cm. of solution was obtained on standing overnight, this value showing no decrease on standing for a further 8 hours. Taking this as the true osmotic pressure, we obtain 2.17 as the value of π/c, indicating a molecular weight of approximately 11,400.

A reliable value for M is thus obtained only at the expense of speed in determination. No technique has yet been developed by which molecular weights of this order of magnitude may be quickly and accurately determined for unfractionated polymers, and the region 5000-10,000 must at present be regarded as a lower limit for osmotic work on high polymer systems.

DISCUSSION

Table IX summarizes the results for the μ values found in the above experiments.

TABLE IX. Values of μ for Various Systems

Polymer	Solvent	Temperature °C.	μ
Polyvinyl acetate	Benzene	20	0.41-0.44
	Ethyl acetate	20	0.415
Polymethyl methacrylate	Benzene	16	0.46-0.48
Polyvinyl xylene	Benzene	24	0.47
Polyacrylonitrile	Dimethylformamide	13.5	0.12-0.29
Polyacenaphthylene	Benzene	25	0.475

In determining molecular weights it is obviously best to employ a solvent for which μ is constant in the dilute solution region, such solvents being benzene for polyvinyl xylene and polyacenaphthylene, and ethyl acetate for polyvinyl acetate. In the case of rubber, Gee (11) obtains curvature of the π/c - c plot using benzene as solvent, while Meyer (12) reports a linear plot using toluene. In this connection it is interesting to note that the heats of dilution, ΔH_1, of rubber in benzene and toluene have been measured (13). The quantity of $\Delta H_1/v_2^2$ (where v_2 is the volume fraction of rubber in the solution) is small for toluene solutions but far from negligible in the case of benzene as solvent, and a possible explanation is provided for the linearity of the π/c - c plot in toluene. In such a case, deviations of the polymer solutions from ideality would be due almost entirely to nonideal entropy of mixing, and the condition of random mixing assumed in the statistical calculation of the entropy of dilution, ΔS_1, would be obeyed, so that the π/c - c curve would have the linear form predicted by the theory.

These considerations apply also to the results for polyvinyl acetate in benzene and ethyl acetate. For the polyvinyl acetate ethyl acetate system, the heat of dilution has been shown to be zero by direct measurement (14). Attempts to check this, and to determine the heat of dilution for the system polyvinyl acetate-benzene by measuring the temperature effect of osmotic pressure were not successful owing to difficulties encountered in operating the osmometer at elevated temperatures. These difficulties were associated with (a) holding the temperature of the osmometer sufficiently constant and (b) the formation of air bubbles in the cell liquids leading to fluctuations in the meniscus levels. To overcome these difficulties, a further modified Fuoss-Mead osmometer designed for immersion in the thermostat liquid is under construction and will be described later.

Acknowledgment

We should like to thank The Distillers' Company Ltd. for the award of a Postgraduate Scholarship to one of us (C.R.M.) which made it possible to carry out these researches.

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Synopsis

Bacterial cellulose membranes have been used successfully to measure the osmotic pressures of a number of high polymer-solvent systems. The dynamic method of Fuoss and Mead has been used in most cases, but for polyvinylxylene in benzene the rate curves are not symmetrical since the solvent passes through the membrane faster from the solution side. The molecular weight values for two polyvinyl acetates agree well with the calculated kinetic values, and for polyethyl sebacate the value obtained agrees with that found by end-group titration. Values of the Huggins "constant" μ are given for various systems.

Résumé

Des membranes de cellulose bactérienne ont été employées avec succès pour déterminer les pressions osmotiques d'un certain nombre de systèmes polymères-solvants. Dans la plupart des cas, la méthode dynamique de Fuoss et Mead a été utilisiée; pour le polyvinylxylène dans le benzène les courbes de vitesses ne sont toutefois pas symétriques parce que le solvant, provenant de la solution, passe plus rapidement à travers la membrane. Les valeurs des poids moléculaires de deux acétates de polyvinyles correspondent aux valeur cinétiques calculées; pour le polysébaçate de l'ethylène glycol la valeur obtenue correspond à celle déterminée par titration des groupes terminaux. La constante μ de Huggins a été établie pour divers systêmes.

Zusammenfassung

Bakterielle Cellulosemembrane werden mit Erfolg für Messungen einer Reihe von Polymer-Lösungsmittelsystemen benützt. In der Mehrzahl dieser Fälle wurde die Fuoss-Meadsche Methode (dynamische Methode) benützt. Fur Polyvinylxylol in Benzol sind die Geschwindigkeitskurven nicht symmetrisch, da das Lösungsmittel von der Lösungsseite rascher durch die Membrane dringt. Die Molekulargewichtswerte für zwei Polyvinylazetate stimmen gut mit den berechneten kinetischen Werten überein, und für ein Polysebacinsäure Äthyl-Ester-Polymerisat ist der Wert dem durch Endgruppen-Titrierung erhaltenen gleich. Die Werte der Hugginschen "Konstanten" werden für die verschiedenen Systeme gegeben.

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Specific Refractivity-Temperature Data for Polyvinyl Acetate and Polybutyl Acrylate *

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The possibility that specific refractivity (R)-temperature data for polymers show a change of slope at the second-order transition temperature, T_m, has been considered (1), but the lack of necessary data has not permitted a careful analysis of the possibility. In this paper we wish to present specific refractivity-temperature data for polyvinyl acetate over the range 0° to 70°C. and through the transition temperature, 28°C., for polybutyl acrylate over the range 5° to 57°C., all above the transition temperature, -70°C. Figure 1 shows the temperature dependence of refractive index and specific volume for polyvinyl acetate, Sample II. The specific refractivity-temperature data, calculated from both the Lorentz-Lorenz and Eyckman equations, is given in Table II. These data show that for polyvinyl acetate the specific refractivity varies from 0.2337 to 0.2348 (Lorentz-Lorenz) and 0.5198 to 0.5213 (Eyckman). The deviation of ±0.0005 (L-L) and ±0.0007 (E) is close to the experimental accuracy achieved; ±0.0004 (L-L) and ±0.0006 (E). It will be noted, however, that the data, particularly for Sample II, show most of this change occurring above the transition temperature as an increase with temperature. Below 28°C., the specific refractivities are 0.2338 ± 0.0001 (L-L) and 0.5200 ± 0.0002 (E). Above 28°C. the values rise from 0.2339 to 0.2348 (L-L) and 0.5201 to 0.5212 (E).

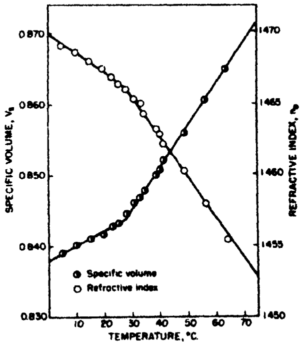

Fig. 1. Temperature dependence of refractive index and specific volume for polyvinyl acetate (Sample II).

The upward trend of specific refractivity above T_m suggested that measurements on another polymer, with T_m below the temperature range being studied, would show an increase clearly in excess of experimental error. Polybutyl acrylate, $T_m = -70^oC.$, was selected. The data for this polymer show an increase in specific refractivity from 0.2533 to 0.2549 (L-L); 0.5638 to 0.5656 (E) in the range from 5^o to 57^oC. The over-all change of 0.0016 (L-L) and 0.0018 (E) is double that observed for polyvinyl acetate. Since it corresponds to approximately twice the temperature interval, a change of the specific refractivity with temperature at the same order of magnitude is indicated. The increase with polybutyl acrylate corresponds to a variation of ±0.0008 (L-L) and ±0.0009 (E) and is outside the experimental error. It is considerably greater than the temperature variation of molecular refraction for hydrocarbons (see Table IV of reference 3). Further experiments over a wider temperature interval which should magnify this increase and assist in establishing the phenomenon conclusively are in progress.

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It is recognized that, as a measure of electron polarizability, the specific refractivity would probably be nearly independent of temperature for polymers just as it is with low-molecular liquids (2,3) provided that the derivation of the Lorenz-Lorentz equation made no assumption contrary to conditions existing in the polymer. The Lorenz-Lorentz equation was derived with reference to the polarizability of an electron in an isotropic medium (3,4). In order to take into account the added force on the electron due to polarization, a spherical cavity having its center at the position of the electron in question was cut out of the medium. The force at the center of this sphere averaged zero, as they would in an isotropic medium. The inadvisability of this assumption has been questioned before (3). In a polymer where the polarizability is referred to a unit of the polymer chain, and this unit is joined by primary valence bonds to similar units at each end, it seems possible that the atomic forces would not be isotropic. The spherical cavity should probably be replaced by an unsymmetrical cavity, perhaps an ellipsoid, to correspond to the nonuniformity of the forces. Moreover, in a polymer the polarizability might conceivably vary as adjacent units change their relative positions through rotations about carbon-carbon bonds, an effect usually associated with temperature changes. The data presented here indicate that below T_m no such revision of the Lorentz-Lorenz derivation is needed. The specific refractivity of the two polyvinyl acetate samples are constant within limits of experimental error below T_m. Sample II shows less variation than Sample I. Confirmation over a wider temperature range would be helpful. Above T_m, however, there remains some possibility that some anisotropic effect, though very small, is involved, perhaps introduced by increased rotation about carbon-carbon bonds above T_m.

EXPERIMENTAL

The polyvinyl acetate, Sample I was prepared as a solid plug, 8 x 30 mm., by polymerization of the purified monomer at $50^oC.$ for 48 hours with 50 mg. benzoyl peroxide per 25 ml. monomer as catalyst. The sample, free of all visible voids, was further heated at $70^oC.$ for 24 hours and then for 100 hours at $85^oC.$ at 5 mm., and stored over phosphorus pentoxide at all times except during measurements.

The polyvinyl acetate, Sample II, was prepared as a solid plug by polymerization of the purified monomer at 40°C. for 72 hours with 50 mg. benzoyl peroxide per 25 ml. monomer. The sample was heated at 70°C. for 10 days and then at 70°C. for 100 hours at 3 mm., and was stored over phosphorus pentoxide. Two identical plugs were used in the volume-temperature measurement to increase the sample size.

The polybutyl acrylate was prepared as a simple plug by polymerization of the purified monomer at 40°C. for 12 days with 50 mg. benzoyl peroxide per 25 ml. monomer as catalyst. The sample was further heated at 65°C. for 5 days, and then for 5 days at 60-70°C. at 2 mm., and was stored over phosphorus pentoxide.

The polyvinyl acetate samples had limiting viscosities, from the plot of N_{sp}/C-C at C=O, in acetone at 25°C. of 1.76 (Sample II) and 2.28 (Sample I). These correspond to molecular weights of 570,000 and 830,000 using the constants previously determined for fractionated polyvinyl acetate (5). A suitable solvent for determining the viscosity of the polybutyl acrylate was not found. Gels were obtained in acetone, toluene, ethyl acetate, and other solvents, indicating that the polymer was of very high molecular weight.

The relative volume-temperature data was determined by a previously described technique (6). The dilatometer was made from precision bore tubing 0.02 inch in diameter, and was checked for uniformity of cross section. The volume increments, which are sufficient to show the transition temperature, were converted to specific volumes, for use in the specific refractivity equation, from the determination of the sample volume at given temperatures.

The refractive index was determined as previously described (7). Three different samples of the plug used in the relative volume measurements of polyvinyl acetate, Sample I, were used. The bulk sample was mounted between the heated prisms, so that practically no pressure was required to form the film. The three samples of polyvinyl acetate, Sample I, gave values of N_D agreeing to ±0.0002, and T_m ±1.0°C.

TABLE I. Physical Data for Polyvinyl Acetate and Polybutyl Acrylate

Measurement	Polyvinyl acetate Sample I	Polyvinyl acetate Sample II	Polybutyl acrylate
Weight of sample, g.	1.6925	2.6927	1.5599
Density, g./ml.[a]	1.181/33°	1.184/28°	1.087/26°
Volume of sample, ml.	1.4331/33°	2.2742/28°	1.4351/26°
Refractive index[b]	1.4667/24°	1.4664/25°	1.4631/30°
Transition temperature, °C.			
From volume/T	30°	28°	—
From refractive index/T	29°	28°	—

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[a] ±0.002. [b] ±0.0003

TABLE II. Specific Refractivity-Temperature Data

T, °C.	ΔV[a]	V_R[b]	V_S[c]	n_D[d]	Specific refractivity Lorentz-Lorenz[e]	Specific refractivity Eyckman[f]
			Polyvinyl Acetate, Sample I			
69.8	0.0358	1.4689	0.8679	1.4535	0.2348	0.5210
64.0	0.0305	1.4636	0.8648	1.4553	0.2348	0.5211
56.9	0.0236	1.4567	0.8607	1.4575	0.2346	0.5210
50.0	0.0167	1.4498	0.8566	1.4598	0.2345	0.5209
44.8	0.0120	1.4451	0.8538	1.4616	0.2346	0.5211
39.9	0.0071	1.4402	0.8509	1.4628	0.2343	0.5207
33.0	0.0000	1.4331	0.8467	1.4648	0.2340	0.5202
30.7	-0.0016	1.4315	0.8458	1.4652	0.2339	0.5200
28.8	-0.0019	1.4312	0.8456	1.4658	0.2341	0.5206
28.0	-0.0027	1.4304	0.8451	1.4659	0.2340	0.5204
26.0	-0.0028	1.4303	0.8451	1.4663	0.2342	0.5207
24.0	-0.0036	1.4295	0.8446	1.4667	0.2342	0.5208
22.0	-0.0044	1.4287	0.8441	1.4669	0.2342	0.5208
20.0	-0.0050	1.4281	0.8438	1.4671	0.2342	0.5208
15.0	-0.0068	1.4263	0.8427	1.4678	0.2342	0.5208
10.0	-0.0084	1.4247	0.8418	1.4683	0.2341	0.5208
5.0	-0.0099	1.4232	0.8409	1.4689	0.2341	0.5209
0.0	-0.0113	1.4218	0.8401	1.4694	0.2341	0.5209
			Polyvinyl Acetate, Sample II			
63.4	0.0546	2.3288	0.8648	1.4554	0.2348	0.5212
56.3	0.0428	2.3170	0.8605	1.4579	0.2348	0.5213
48.4	0.0305	2.3047	0.8559	1.4603	0.2346	0.5210
42.2	0.0200	2.2942	0.8520	1.4621	0.2343	0.5206
40.0	0.0165	2.2908	0.8507	1.4628	0.2342	0.5205
38.7	0.0145	2.2887	0.8500	1.4632	0.2342	0.5205

T, °C.	ΔV[a]	V_R[b]	V_S[c]	n_D[d]	Specific refractivity	
					Lorentz-Lorenz[e]	Eyckman[f]
Polyvinyl Acetate, Sample II (continued)						
34.6	0.0083	2.2825	0.8477	1.4643	0.2340	0.5203
32.9	0.0060	2.2802	0.8468	1.4650	0.2341	0.5204
30.7	0.0040	2.2782	0.8461	1.4653	0.2340	0.5203
28.0	0.0000	2.2742	0.8446	1.4660	0.2339	0.5201
25.1	-0.0035	2.2707	0.8433	1.4664	0.2337	0.5198
22.8	-0.0049	2.2692	0.8427	1.4669	0.2338	0.5199
19.7	-0.0065	2.2677	0.8422	1.4675	0.2339	0.5202
15.0	-0.0092	2.2650	0.8412	1.4680	0.2338	0.5201
10.0	-0.0120	2.2622	0.8401	1.4687	0.2338	0.5202
5.0	-0.0149	2.2593	0.8390	1.4691	0.2337	0.5200
Polybutyl Acrylate						
57.4	0.0329	1.4680	0.9411	1.4541	0.2549	0.5656
50.0	0.0249	1.4600	0.9360	1.4565	0.2547	0.5654
40.0	0.0143	1.4495	0.9292	1.4599	0.2545	0.5652
30.0	0.0040	1.4391	0.9226	1.4631	0.2541	0.5648
20.0	-0.0062	1.4288	0.9160	1.4663	0.2538	0.5644
10.0	-0.0166	1.4185	0.9093	1.4697	0.2536	0.5642
5.0	-0.0217	1.4134	0.9061	1.4712	0.2533	0.5638

---

[a] Volume increment.

[b] Volume of sample.

[c] Specific volume; V_R/sample weight.

[d] Refractive index.

[e] From Lorentz-Lorenz equation: $R = \frac{n^2 - 1}{n^2 + 2} \cdot V_S$

[f] From Eyckman equation: $R = \frac{n^2 - 1}{n + 0.4} \cdot V_S$

A duplicate set of measurements, of both relative volume and refractive index, with a second sample of polyvinyl acetate gave results checking within experimental error as shown in Tables I and II.

Density was determined using a pycnometer, Type A (8), and mercury immersion. The values are given in Table I.

A typical calculation for the data for polyvinyl acetate, Sample I at T = 69.8°C., using the notation previously adopted (6), follows.

Volume of mercury (33°). The polymer sample was weighed and sealed in a dilatometer. The dilatometer with sample was weighed, filled with mercury, and reweighed. Weight of mercury, 30.60 g.; volume of mercury using $d_{33} = 13.514$; $V_m = 2.2643$ ml.

Volume of sample (33°) = Density of polymer at 33°, 1.181 ±0.002; weight, 1.6925g.; volume of polymer, 1.4331 ml.

Volume of glass bulb (33°) = Volume of mercury, 2.2643, + volume of sample, 1.4331, - volume of mercury in column, 0.0359 (height at 33°, 17.70 cm., x cross section, 0.002027 cm.^{2}) = 3.6617 ml.

Height of mercury at 69.8°, 42.20 ± 0.1 cm.

Relative volume (V_R). From:

$$\Delta V = A(x_{t_2} - x_{t_1}) - (t_2 - t_1)(\alpha_m V_m - \alpha_g V_g)$$

where $\alpha_m = 0.1819 \times 10^{-3}$ and $\alpha_g = 0.96 \times 10^{-5}$ and values determined as above.

$$\Delta V = 2.027 \times 10^{-3} (42.20 - 17.70) - 36.8(0.1819 \times 10^{-3} \times 2.2643) - (0.96 \times 10^{-5} \times 3.662)$$

$$\Delta V = 0.04966 - 0.01386 = 0.0358 \pm 0.0001$$

$$V_R = V + \Delta V = 1.4331 + 0.0358 = 1.4689 \ (69.8^\circ)$$

similarly $V_R = 1.4218$ at 0°.

Analysis of error. The values of the refractive index are determined to ±0.0003, about ± 0.02%. These deviations give in turn deviations of ±0.1% in the $(n^2 - 1)/(n^2 + 2)$ term and ±0.12% in the $(n^2 - 1)/(n + 0.4)$ term. The absolute density and specific volume are determined to ±0.2%, but this deviation is eliminated from the relative values. The relative volume is determined to ±0.001, or 0.07%, as limited by the reading of the height of the mercury column to ±0.1 cm. From these deviations the maximum deviation in specific refractivity is ±0.0004; 0.17% for the Lorentz-Lorenz value and ±0.0006; ±0.11% for the Eyckman value. The check runs with polyvinyl acetate give values which are within these limits. The maximum deviation, between the 5° values of 0.2341 and 0.2337, is ±0.09% for the Lorentz-Lorenz value.

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Synopsis

Refractive index-temperature and volume-temperature data for polyvinyl acetate and polybutyl acrylate have been determined and used to calculate the specific refractivity as a function of temperature by the Lorentz-Lorenz and the Eyckman equations. The results show a variation of specific refractivity with temperature which exceeds experimental error. The variation is evident as an increase of specific refractivity with temperature above T_m and suggests experiments which will show the increase more clearly. A theoretical justification for the increase of specific refractivity with temperature in polymers is discussed.

Résumé

Les variations de l'indice de réfraction et du volume de l'acétate de polyvinyle et du polyacrylate de butyle en fonction de la température ont été déterminées; elles ont permis le calcul de la réfractivité spécifique en fonction de la température, suivant les équations de Lorentz-Lorenz et de Eyckmann. La variation de la réfractivité spécifique en fonction de la température dépasse les erreurs de mesures, et consiste en une augmentation de réfractivité au dela de la température de fusion; elle suggère des expériences plus définitives. Une justification théorique pour cette augmentation de réfractivité spécifique avec la température est discutée dans le cas des polymères.

Zusammenfassung

Refraktions index-Temperatur und Volumen-Temperatur Werte für Polyvinylazetat und Polybutylakrylat werden gemessen und zur Berechnung der spezifischen Refraktivität als Funktion der Temperatur mit Hilfe der Lorentz-Lorenz und Eyckman Gleichungen benutzt. Die Ergebnisse zeigen eine Abweichung der spezifischen Refraktivität mit Temperatur die nicht auf experimentelle Fehler zurückzuführen ist. Die Abweichung zeigt sich als ein Ansteigen der spezifischen Refraktivität mit steigender Temperatur, oberhalf von T_m und regt Experimente die dieses Ansteigen klarer zeigen, an. Eine theoretische Erklärung für das Ansteigen der spezifischer Refraktivität mit Temperatur in hochmolekularen Stoffen wird erörtert.

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Polymerization of Isobutene Catalyzed by Boron Trifluoride

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The effect of Friedel-Crafts catalysts on isobutene and di-isobutene has been studied by Thomas et al. (1). Recent work (2) on these reactions has led to the conclusion that a third component, other than the Friedel-Crafts catalyst and the monomer, is necessary for an appreciable reaction rate to occur. In particular, it has been shown that rapid polymerization of isobutene does not occur when pure isobutene vapor is mixed with pure boron trifluoride gas; rapid polymerization occurs under these conditions only in the presence of a co-catalyst (3). In this paper we shall describe these experiments together with later work and discuss the significance of the results obtained.

EXPERIMENTAL

Materials

Isobutene was kindly given to us in cylinders by Messrs. Imperial Chemical Industries Ltd. (Billingham Division). It was purified in a high vacuum apparatus by distillation from -80°C. to liquid air temperature followed by two further distillations over a sodium film heated at 70-80°C. The last 5 to 10% of the residue was discarded each time.

Boron trifluoride was kindly given to us in cylinders by Messrs. Imperial Chemical Industries Ltd. (Billingham Division), and by the U. S. Rubber Co., Passaic, N. J. It was purified by several distillations in vacuo from -80°C. to liquid air temperature.

Apparatus and Experimental Method

The reaction vessel (Fig. 1) consisted of a liter bulb (R) to which 10 ml. pendant bulbs (A, B, and C) were connected by means of capillary tubing. These small bulbs could be isolated from the large bulb (R) by means of the 1-mm. bore taps (T_A, T_B, and T_C). The pressure in the reaction vessel R could be measured to 0.2 mm. by a manometer attached at M. The reaction vessel was connected to the high vacuum system by the tap T_1.

The purified materials required in each experiment were distilled in turn into the reaction vessel and their pressures measured on the manometer with tap T_1 closed. After measuring the pressure in the known volume R, each component was condensed into a liquid air-cooled pendant bulb, isolated by closing the appropriate tap, and stored in the condensed state until required in the reaction. The various gases were reintroduced into the vessel R by warming each of the small bulbs in turn to room temperature and then allowing the enclosed gas to expand into the reaction vessel. The order of mixing was arranged so that the gases already in bulb R were at a considerably lower pressure than the initial pressure of the incoming gas. Since the last component to be added was usually boron trifluoride, at a high pressure, the final mixing was very rapid. In those experiments which resulted in reaction, the polymer produced was a liquid and had a negligible vapor pressure at room temperature (less than 0.2 mm). Thus the progress of the reaction could be followed by the fall in pressure recorded on the manometer. No attempt was made to thermostat the reaction vessel, and so all the reactions were carried out at room temperature.

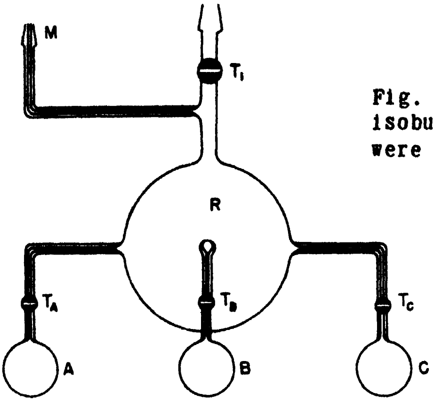


Fig. 1. Reaction vessel in which isobutene and boron trifluoride were mixed.

RESULTS

Pure and Unpurified Isobutene

Boron trifluoride, usually 10-15 mm. pressure, was measured in bulb R, and condensed into a pendant bulb where it was isolated from the reaction vessel. Vessel R was pumped out for about 10 minutes and 100 to 110 mm. pressure of isobutene was then introduced. The bulb containing the boron trifluoride was then warmed up to room temperature, the resulting pressure being 1000-1500 mm. in the closed bulb. The boron trifluoride was then allowed to expand into the isobutene in vessel R.

It was found that when unpurified isobutene taken directly from the cylinder was used, a rapid reaction occurred on introducing boron trifluoride (Fig. 2, curve A). This reaction was accompanied by the formation of a dense fog throughout the reaction vessel. The polymer produced was a liquid which streamed down the vessel walls. When boron trifluoride was introduced into purified isobutene, however, the resulting pressure was found to be the sum of the individual pressures of boron trifluoride and isobutene, and only a slow reaction took place (Fig. 2, curve B). This very slow reaction was not accompanied by any fog but led to the formation of small droplets of liquid polymer on the vessel walls. It was found that the more rigorously the isobutene was purified the slower was this reaction, and we attribute this slow reaction to residual impurity still present in the isobutene.

Whenever a practically nonreacting boron trifluoride - isobutene mixture was condensed into an external trap cooled in liquid air, and the cooled mixture then allowed to return to room temperature, it was found that the isobutene fraction of the gas mixture had polymerized to give a white solid. The boron trifluoride reaction of the gas mixture could be distilled back unchanged into R, where its pressure was found to be equal to the pressure of boron trifluoride taken initially. In all the experiments described above it was found that within the accuracy of our technique the polymerization reaction did not consume any boron trifluoride.

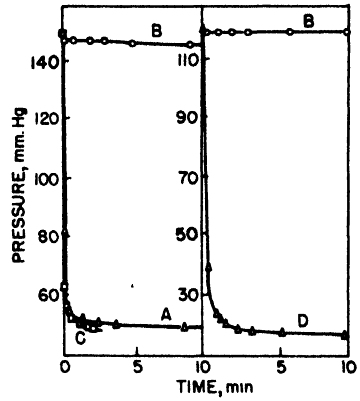


Fig. 2. Polymerization of isobutene by boron trifluoride. A, unpurified isobutene; B, distilled isobutene; C, distilled isobutene plus 1% residue vapor; D, distilled isobutene plus 0.1% water vapor.

Pure Isobutene Mixed with Distillation Residue

On distilling off the excess isobutene at -80°C. from the residue rejected in the first distillation of the isobutene purification process, a white solid was obtained which liquified on warming to room temperature. Mixtures of about 100 mm. of purified isobutene and 1 mm. of the vapor of this residue were made in the reaction vessel R. When boron trifluoride was introduced into such mixtures a dense fog was formed, and rapid polymerization of the isobutene occurred (curve C, Fig. 2). The above experiments prove that under these conditions the rapid polymerization of isobutene by boron trifluoride requires the presence of a third component, or co-catalyst, in addition to the monomer and the Friedel-Crafts catalyst.

Identification of the Residue from Isobutene Purification

The colorless liquid isolated from the residue described above was identified as water by melting point and vapor pressure measurements. Thus in the foregoing experiments the co-catalyst was water. This was confirmed by the fact that rapid reaction occurred when pure isobutene containing 0.1% water vapor was used (curve D, Fig. 2).

Reaction of Isobutene in the Presence of Other Co-catalysts

We have found that tert-butyl alcohol and acetic acid are also effective co-catalysts for this reaction. The effect of these substances on the polymerization of gaseous isobutene was studied as follows. Mixtures of the co-catalyst and isobutene were prepared in the reaction vessel R by introducing them in this order, and the boron trifluoride was then added. The initial pressures of isobutene and boron trifluoride were of the order of 100 mm. and 15 mm., respectively, while the pressure of co-catalyst was very small in this series of experiments (<0.1 mm.). The small quantities of co-catalyst used in these experiments were measured out as follows. The large bulb R and one of the small pendant bulbs was filled with co-catalyst vapor at the desired pressure (which was within the range 1 to 10 mm.). The pendant bulb was then isolated, the reaction vessel pumped out, and the co-catalyst distilled from the pendant bulb into the reaction vessel. Knowing the volume ratio of bulb R to pendant bulb, the total quantity of co-catalyst in R was then determined. This total quantity includes that fraction of the co-catalyst adsorbed on the walls of reaction vessel R. In this paper we refer to the total quantity of co-catalyst present in the system by the pressure it would exert if it were completely in the gas phase.

Since water was proved to be such an effective co-catalyst for this reaction, the acetic acid and tert-butyl alcohol were purified by fractional crystallization and fractional distillation under high vacuum conditions. The tert-butyl alcohol was first treated with sodium. The sample finally used as the source for all the small quantities required in the experiments was collected in a tube under high vacuum and isolated by means of a tap when not required. In order to establish the purity of this material without exposing it to the atmosphere, small samples were collected and sealed under vacuum before and after the distillation of the experimental sample. The melting points were measured and found to agree closely with the literature values. The quantity of water present in either the acetic acid or the tert-butyl alcohol was thus shown to be less than 0.5%, and the effect of these substances as co-catalysts was far greater than could possibly be attributed to any such small quantity of water impurity.

It was found that 0.01 mm. pressure of co-catalyst in 100 mm. pressure of isobutene gave a slow reaction, while 0.1 mm. pressure resulted in a very rapid polymerization. The rapid reactions were always accompanied by a dense fog and the production of liquid polymer which streamed down the walls of the vessel. In the case of the slow reactions, fog was not produced on adding boron trifluoride, although on many such occasions an immediate filming of the reaction vessel wall was observed.

The marked increase in rate over the range of co-catalyst pressure, 0.01 mm. to 0.1 mm., appeared to be accompanied by a change in the nature of the reaction. The slow reactions were first order in isobutene, but the pressure-time curves for the fast reactions showed a sudden drop in rate during the course of the reaction. This effect may be seen in Figure 3, which shows the change in polymerization rate on varying the tert-butyl alcohol pressure from 0.01 to 0.1 mm.

The dependence of the reaction speed on the amount of catalyst present was found for both water and acetic acid to be very similar to that observed for tert-butyl alcohol.

In recent experiments we have found that diethyl ether can act as a co-catalyst for this reaction, and that its efficiency is very low compared with that of water, tert-butyl alcohol, and acetic acid. (To produce a given reaction rate the pressure of ether required is at least ten times that necessary in the case of the other co-catalysts.) Topchiev and Tumerman have also used boron trifluoride etherate to polymerize isobutene in the gas phase (4).

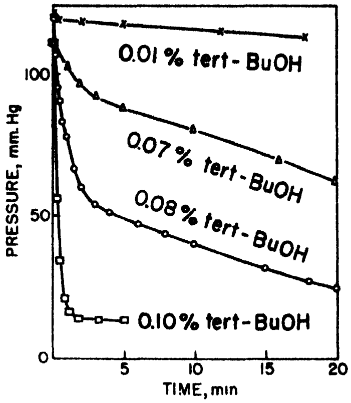


Fig. 3. Polymerization of isobutene containing varying amounts of tert-butyl alcohol.

Effect of Co-catalyst on First-Order Constant of Slow Reaction

To determine the effect of the co-catalyst on the first-order constant of the slow reaction, isobutene was used which had been distilled once only in order that the small amount of co-catalyst remaining would give a moderate reaction rate. 250 mm. of this isobutene were introduced into R and separate 50-mm. portions of this sample were isolated by condensing in turn into three of the pendant bulbs. The reaction was started by introducing 15 mm. boron trifluoride into the remaining 100 mm. of this isobutene in R, and when about half of this had polymerized, a further quantity of isobutene was introduced from one of the pendant bulbs. This was done three times in all. On each occasion an increase in the reaction rate was observed, although the initial isobutene pressures were comparable (Fig. 4). The slopes of the first-order plots for each stage of the reaction (Fig. 5) were found to increase with increase in the total quantity of isobutene which had been added in that and the previous stages of the experiment. (Table I gives the results for two experiments, A and B. Figures 4 and 5 illustrate experiment A.) Since the addition of each sample of iso-

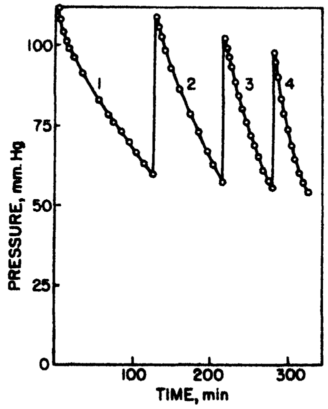


Fig. 4. Increase in rate of reaction as successive samples of isobutene are introduced into reaction vessel.

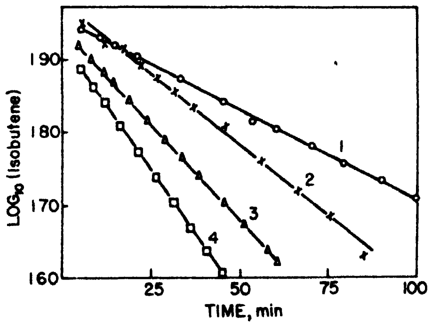


Fig. 5. First-order plots for reaction of isobutene after successive samples have been introduced. (See Table I, A, for ratio of total isobutene to initial isobutene and for ratio of first-order constant to initial constant.)

butene introduces a further quantity of co-catalyst into the reaction vessel, these results show that the first-order constant increases with increase in the total quantity of co-catalyst present.

TABLE I. Effect of Co-catalyst on the First-Order Constant

Stage of experiment	Total quantity of isobutene added (mm. pressure in R).	Ratio of total isobutene to initial isobutene	First-order constant, min.$^{-1}$	Ratio of first-order constant to initial constant
		A		
1	96	1	2.5×10^{-3}	1
2	146	1.5	3.8	1.5
3	192	2.0	5.2	2.1
4	234	2.5	7.1	2.9
		B		
1	100	1	1.9×10^{-3}	1
2	148	1.5	2.7	1.4
3	248	2.5	6.1	3.2

Necessity of Excess Boron Trifluoride for the Fast Reaction When Acetic Acid is Co-catalyst

4 mm. boron trifluoride was introduced into a mixture of 100 mm. isobutene and 6 mm. acetic acid. Although the co-catalyst concentration was 50 times that required (0.1 mm.) to give a fast reaction in the presence of excess boron trifluoride, the observed rate was quite slow (Fig. 6). On the further addition of 15 mm. boron trifluoride to this slowly reacting mixture, the reaction became very rapid, and the final pressure (5 mm. BF$_3$), indicated that altogether 14 mm. of boron trifluoride had been removed by the 6 mm. of acetic acid. Since

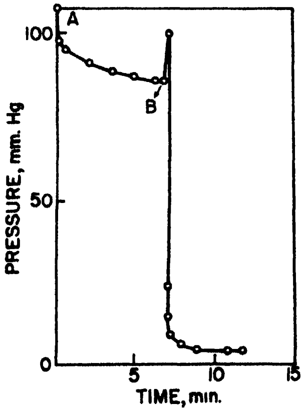


Fig. 6. Necessity for excess boron trifluoride for the fast reaction when acetic acid is the co-catalyst: A, 4 mm. BF$_3$ is added to 100 mm. isobutene plus 6 mm. CH$_3$COOH; B, an additional 15 mm. BF$_3$ is added.

acetic acid is largely dimerized in the vapor phase, this indicates that in the final stage of this reaction some complex of composition BF_3 (CH_3COOH) must be present).

Addition Complex of Co-catalyst with Boron Trifluoride

Experiments were performed in which excess boron trifluoride was added to 5 to 10 mm. pressure of co-catalyst either alone or mixed with purified isobutene in the reaction vessel R. In those cases in which isobutene was present, a very fast reaction accompanied by a dense fog was observed, and the final pressure of boron trifluoride was appreciably smaller than the initial value due to removal of boron trifluoride by the co-catalyst added to the system. When no isobutene was present a beam of spray was observed across the vessel R from the point of entry of the boron trifluoride into the co-catalyst, and this spray settled immediately on the surface of the vessel. (The density of this spray was much less than that of the fog obtained when isobutene was present.) There was an immediate drop in pressure due to the removal of boron trifluoride and co-catalyst, and the residual pressure was that of excess boron trifluoride. The results obtained in these experiments are given in Table II.

TABLE II. Composition of Co-catalyst Boron Trifluoride Complex

Co-catalyst	Pressure in R, mm.					
	Iso-butene	Co-catalyst	Initial BF_3	Final BF_3	BF_3 consumed	BF_3 consumed/ co-catalyst
Water	98	11.5	47.0	34.5	12.5	1.1
Water	105	10.0	50.8	39.0	11.8	1.
Water	62	10.0	53.6	42.3	11.3	1.1
tert-Butyl alcohol	-	5.0	29.5	24.0	5.5	1.1
tert-Butyl alcohol	-	4.0	24.1	19.6	4.5	1.1
Acetic acid.......	100	6.0	19.0	4.6	14.4	2.4
Acetic acid.......	-	6.0	15.0	0.8	14.2	2.4
Acetic acid.......	-	4.0	15.0	6.0	9.0	2.3
Acetic acid.......	-	4.5	15.0	5.0	10.0	2.2

In the case of water and tert-butyl alcohol, it was found that the co-catalyst combined with boron trifluoride in equal proportions as measured by the fall in pressure. For acetic acid, it was found that there was an initial rapid fall in pressure followed by a slow consumption of boron trifluoride. Since acetic acid vapor is highly dimerized, the composition of the boron trifluoride - acetic acid addition complex finally obtained was probably BF_3 $(CH_3.COOH)$. This final composition was attained only slowly, and in the presence of excess boron trifluoride. The complex crystallized on the walls of the reaction vessel. These crystals were stable only in the presence of excess boron trifluoride; on removing the excess boron trifluoride from above the crystals, either by pumping it away or by condensing it into another vessel, the crystals slowly liquified and decomposed with the evolution of a gas. This showed that the compound $BF_3(CH_3.COOH)$ had a dissociation pressure of boron trifluoride at room temperature, and the removal of the excess boron trifluoride from the system caused the crystalline complex to decompose, probably to give the liquid complex $BF_3(CH_3.COOH)_2$ according to the equation:

$$2BF_3(CH_3.COOH) \longrightarrow BF_3(CH_3.COOH)_2 + BF_3$$

Meerwein (5) has reported that boron trifluoride forms two complexes with acetic acid. First, a fairly stable liquid, $BF_3(CH_3.COOH)_2$, b.p. 53-54°C. (10 mm.), and, in the presence of excess boron trifluoride, an unstable crystalline compound, $BF_3(CH_3.COOH)$, m.p. 23-24°C. We have prepared a crystalline complex by saturating about 10 cc. acetic acid with boron trifluoride. The composition of this complex was shown to be $BF_3(CH_3.COOH)$ by weighing both the initial acetic acid and the final complex. The melting point of this compound was found to be 38°C. under its own dissociation pressure.

Polymerization of Isobutene Using Preformed Boron Trifluoride Acetic Acid Compound as Catalyst

$BF_3(CH_3.COOH)$, the crystalline boron trifluoride - acetic acid complex, was prepared in the reaction vessel R, and the excess boron trifluoride was condensed off into an external trap. The decomposition of the crystals due to the removal of the excess boron trifluoride was a slow process, and it was possible to introduce pure isobutene from a pendant bulb before any appreciable change in the crystals had occured. The isobutene polymerized rapidly (Fig. 7A) without the production of any fog, and liquid polymer was observed only at the points where crystals had developed. The reaction vessel was then pumped out for thirty minutes, and a further sample of pure isobutene was introduced into R. This sample polymerized at a reduced rate (Fig. 7B).

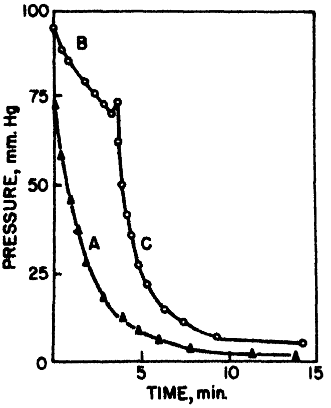


Fig. 7. Reaction of isobutene on boron trifluoride - acetic acid complex: A, reaction of isobutene on crystals of $BF_3.CH_3COOH$; B, reaction of isobutene after crystals had been pumped out for 30 minutes; C, acceleration of this slower reaction when BF_3 is introduced.

Introduction of boron trifluoride accelerated this slower reaction (Fig. 7C) and produced a fog. This fog was probably due to the fact that vapor of the $BF_3(CH_3.COOH)_2$ complex present in the gas space was converted to the crystalline complex, $BF_3(CH_3COOH)$, on introduction of excess BF_3. From these experiments it was concluded that the excess boron trifluoride necessary for the occurrence of the fast reaction is required in order to produce and stabilize the $BF_3(CH_3COOH)$ complex (which appears to be much more active than the complex $BF_3(CH_3COOH)_2$) in accordance with the equilibrium:

$$BF_3(CH_3COOH)_2 + BF_3 \rightleftharpoons 2BF_3(CH_3COOH)$$

Experiments Showing that the Reaction at Room Temperature Does not Occur in the Gas Phase

As described above, in the presence of crystals of $BF_3(CH_3COOH)$ the polymerization of isobutene gas occurred only on the surface of the crystals, the remaining portion of the reaction vessel wall remaining free from polymer. This indicates that under these conditions the polymerization is not occurring in the gas phase. We shall now describe experiments with support this conclusion.

APPARATUS

The apparatus consisted of two 1-liter reaction bulbs (R_1 and R_2) connected through a 2-mm. bore tap (T_2) and provided with mercury manometers (M_1 and M_2). R_1 had 10-ml. pendant bulbs attached, each bulb being equipped with a 1-mm. bore tap. The bulb R_1 was attached to the main high vacuum system.

EXPERIMENTAL

The apparatus was pumped out for about an hour prior to these experiments and during this period both the manometers and the whole of bulb R_2 were heated to remove traces of water adsorbed on the glass walls. Cleaning of the vessel surfaces was found to be particularly important in the case of slow reactions because of their sensitivity to moisture. It was only by taking great care in this way with bulb R_2 and manometer M_2 that the subsequently described nonreacting gaseous mixtures of isobutene and boron trifluoride were obtained. Slow reactions were started in R_1 with T_2 closed, using water as a co-catalyst and the mixing technique previously described. After following the reaction in R_1 for some time, tap T_2 was opened and the gas mixture was expanded into the previously evacuated vessel R_2, when the pressures in R_1 and R_2 were followed separately by the manometers M_1 and M_2.

The mixture of isobutene and boron trifluoride which was isolated in R_2 by this method was found to be nonreacting, while the isobutene in R_1 reacted to completion. Figure 8 shows the result of an experiment in which, 17 $^1/_2$ hours after the initial expansion from R_1 to R_2 (during which time the isobutene in R_1 had reacted almost completely), the nonreacting mixture in R_2 was allowed to expand back into R_1 and the bulbs again isolated. The isobutene now reacted in R_1, curve A', but the pressure in R_2 again remained steady, curve B'. These experiments lead to the conclusion that this reaction does not occur in the gas phase, all the active complex remaining in R_1 on expansion. The first-order plot given by the reaction in R_1 (curve C, Fig. 8) shows that the activity of the catalyst remains constant over the long period of the reaction.

With small concentrations of co-catalyst, expansion from R_1 to R_2 only 30 seconds after the introduction of BF_3 into R_1 gave a nonreacting mixture in R_2. This shows that the complex either settled very rapidly, or that in the cases where only small quantities of co-catalyst were used the complex was formed initially on the vessel wall. This could explain the filming of the wall which has been referred to earlier.

Immediate expansion (that is, after about 2 seconds) of a system containing a high concentration of co-catalyst resulted in a fast reaction in R_1 and a much slower one in R_2. Only a small fraction of the fog produced in R_1 (on admitting the boron trifluoride) passed into R_2. It appears, therefore, that the bulk of the complex is deposited very rapidly on the vessel wall. This process is probably accelerated by the formation of droplets of polymer on the small particles of complex.

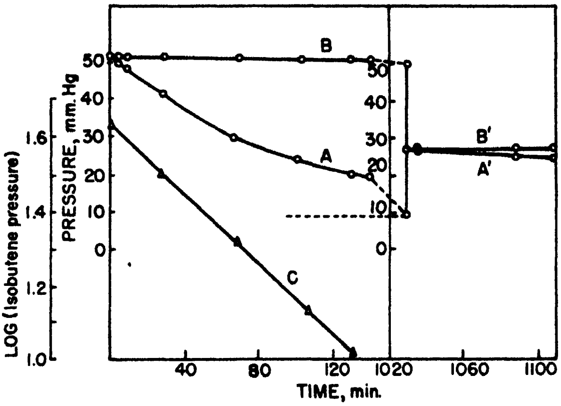


Fig. 8. Expansion experiments to show that the reaction does not occur in the gas phase.
A: Isobutene remaining in vessel R_1 continues to react.
B: Isobutene expanded into vessel R_2 does not react.
A′: Isobutene expanded back from R_2 into R_1 again reacts.
B′: Isobutene remaining in vessel R_2 does not react.
C: First-order plot for the reaction illustrated by curve A.

It was found that even the completely unreactive gaseous mixtures of isobutene and boron trifluoride obtained in R_2 by the expansion from R_1 of slowly reacting mixtures gave a solid polymer on condensing by means of a liquid air cooled pad on the vessel wall and allowing to warm up to room temperature.

In recent experiments we have found that when isobutene and boron trifluoride are still more rigorously purified they can be mixed, condensed by liquid air, and allowed to warm up to room temperature without the isobutene being polymerized. When laboratory air is introduced into the system containing the liquid air cooled mixture, polymerization to a solid high molecular weight polymer occurs on allowing the mixture to warm up.

The $BF_3.H_2O$ complex, which has a negligible boron trifluoride pressure at -80°C., was found to be catalytically active at this temperature and converted isobutene to solid high molecular polymer.

Examination of the Polymer

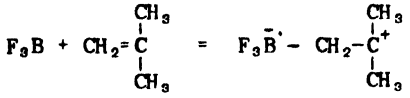
The product of the room temperature polymerization reaction described in this paper is a colorless mobile liquid with a vapor pressure of less than 0.2 mm. The accumulated product of the polymerization of successive batches of isobutene was examined. No attempt was made to determine the molecular weight distribution for this material, but solutions were made in benzene and the freezing point depression measured. In this way a value of 278 was obtained for the molecular weight of a sample of polymer prepared by the same method as that used in the reaction experiments. The refractive index of this sample was also measured and a value of 1.4581 was found for n_D^{20}. The corresponding values for the olefin $C_{20}H_40$ are 280 and 1.4600, respectively. Samples of polymer were also left in contact with a brominating solution at room temperature for various times. (The brominating agent was a methanol solution of bromine saturated with sodium bromide (6)). The excess bromine was titrated using potassium iodide and sodium thiosulfate. Any hydrogen bromide liberated by substitution was determined by the addition of potassium iodate and titration of the liberated iodine with thiosulfate. It was found that bromination of the polymer was a slow process; two hours were required for the removal of an amount of bromine corresponding to one double bond per molecule. It was also found that all the bromine taken up by the polymer was absorbed by substitution and not by addition.

DISCUSSION

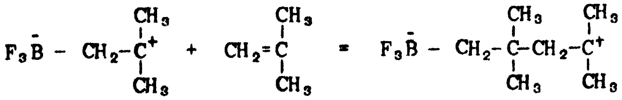
Introduction

Whitmore (7) has discussed the polymerization of olefins by acid catalysts and has proposed a general theory for the mechanism of these reactions. This involves the addition of a proton to one end of the olefin double bond to give a carbonium ion which can then give rise to a polymerization chain process. This process can be terminated by the elimination of a proton from the gorwing polymer molecule.

Polymerization by Friedel-Crafts catalysts has been discussed by various authors (8). According to Hunter and Yohe (8a) and Price (8b) the catalyst molecule adds on to the olefin double bond to give a carbonium ion which can initiate the polymerization chain process, for example:



$$F_3B + CH_2{=}\overset{CH_3}{\underset{CH_3}{C}} = F_3\bar{B}-CH_2-\overset{CH_3}{\underset{CH_3}{C^+}} \qquad (1)$$



$$F_3\bar{B}-CH_2-\overset{CH_3}{\underset{CH_3}{C^+}} + CH_2{=}\overset{CH_3}{\underset{CH_3}{C}} = F_3\bar{B}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C^+}} \qquad (2)$$

This mechanism would result in a polymerization rate determined by the concentrations of boron trifluoride and isobutene. The fact that isobutene vapor and boron trifluoride gas can be mixed to give a nonreacting mixture, the pressure of which is equal to the sum of the pressures of the individual gases, shows, however, that under these conditions there is no addition of the two molecules in the way represented by equation 1. For the reaction to proceed, a co-catalyst-inactive itself - is required as well as the boron trifluoride.

Houtman has reported that traces of water are not essential for the polymerization reaction of isobutene with boron trifluoride and aluminium chloride under conditions where high molecular weight products are formed, although he finds that the reaction proceeds more slowly when working under dry conditions (8f).

Our recent experiments referred to above show that a co-catalyst is necessary for the rapid low-temperature, high molecular weight polymerization of isobutene by boron trifluoride.

Kinetics of the Reaction

The boron trifluoride and the co-catalyst combine to form a complex. In the particular case of acetic acid, the polymerization of isobutene proceeds rapidly in the presence of $BF_3.CH_3COOH$ crystals, and the fact that the reaction does not occur in the gas phase as demonstrated by this experiment has been confirmed by experiments in which the co-catalyst was water by expansion of the reacting gas into a second volume in which the expanded gas does not react.

The fog that is produced initially when the gaseous reactants are mixed to give a fast reaction is, we think, due to the fact that the molecules of boron trifluoride - co-catalyst complex first produced in the gas space aggregate to form particles on which the liquid polymer is produced. In the case in which isobutene is introduced into the reaction vessel containing crystals of $BF_3.CH_3COOH$ on the vessel walls, no fog is produced, since in this case there are no particles of catalyst complex distributed throughout the reaction vessel space.

Since the reaction, under the conditions described in this paper, is not occurring in the gas phase, it is difficult to interpret the pressure-time curves in terms of reaction kinetics. Even in the slow reactions, where first-order constants are obtained which increase with increase in the amount of co-catalyst present, it is difficult to know to what process this first-order constant refers, since after the first stages of the reaction, the surface of the catalyst complex will be covered with a layer of liquid polymer in which some of the monomer and catalyst will dissolve so that reaction may be taking place in solution.

In connection with these experiments, however, there are two important points: (a) that the first-order relationship persists with time; and (b) that the first-order constant increases with successive additions of co-catalyst. From these facts we conclude that the activity of the catalyst remains constant over long periods of time.

The Initiation of Polymerization

The fact that the activity of the catalyst does not decrease as the polymerization reaction proceeds indicates that the mechanism of this reaction does not involve the permanent removal of any group from the catalyst complex. This point is further emphasized by the fact that 0.01-mm. pressure of water vapor is more than sufficient to cause the complete, although very slow, polymerization of 100-mm.

pressure of isobutene. Thus, one water molecule can be effective in the polymerization of at least 10,000 molecules of isobutene. Since there are, on the average, five isobutene units in the polymer molecule, this means that one water molecule can be effective in the production of at least 2000 polymer molecules. (The reaction of liquid di-isobutene also requires a small quantity of co-catalyst and gives low-molecular products (2). From experiments on the stannic chloride polymerization of *N*-butyl vinyl ether, Eley and Pepper (8d) conclude that one molecule of stannic chloride may start a number of chains. R. L. Meier (private communication) has found that in the polymerization of 2-butene by aluminum chloride, as many as 50-100 polymer molecules may be produced for each aluminium chloride molecule used.) At low temperature, high-molecular polyisobutene is formed, so that under these conditions the mechanism of reaction must be a chain process. We shall thus discuss the room temperature reaction in terms of the same chain mechanism. The chain process must occur by the addition to the end of the monomer double bond of a particle from the catalyst complex (e.g., a hydrogen) which can be returned later to the complex residue or to another monomer molecule from a different part of the polymer molecule. In this way the activity of the catalyst would be constantly regenerated throughout the reaction. The product obtained at room temperature contains an average of five isobutene units, and this strongly suggests that, under these conditions, the chain length is two units only. This we conclude from the fact that, when di-isobutene (i.e., two isobutene units) is treated with boron trifluoride, the product contains practically nothing of higher molecular weight than $C_{16}H_{32}$, (i.e., four isobutene units) (9).

Chain Mechanism

(a) Radical Mechanism

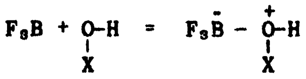
A radical polymerization chain could be initiated by the transfer of a hydrogen atom from the boron trifluoride co-catalyst complex $F_3BO\genfrac{}{}{0pt}{}{X}{H}$ to the double bond to give a free radical, which could then give rise to a free radical polymerization chain. If termination of this chain occurred by the transfer of a hydrogen atom from the active end of the growing chain back to the F_3BOX residue, this would lead to that constancy of catalyst activity with time which is observed experimentally.

This transfer of a hydrogen atom from the catalyst complex $F_3BO\genfrac{}{}{0pt}{}{X}{H}$ to the isobutene molecule will be a very endothermic process. The hydrogen atom affinity of isobutene is 42 kcal. (3b), whereas the energy of breaking the first O-H bond is H_2O is 118.6 kcal. (10); this gives an endothermicity of about 76 kcal. for this process. Even though the coordination of the boron with the oxygen may reduce this bond strength below its value in water, it is difficult to imagine that it can be reduced sufficiently to give an activation energy which would account for the observed reaction rate.

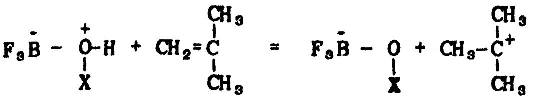
(b) Carbonium Ion Mechanism

The initiation mechanism for Friedel-Crafts catalyzed polymerization of isobutene has been discussed in terms of the transfer of a proton from the co-catalyst complex to the olefin molecule (3b,3e).

(See also references (2) and (3f).) For the case of the boron trifluoride - co-catalyst complex this process may be written (3b):



$$F_3B + \underset{\underset{X}{|}}{O}\text{-}H = F_3\overset{-}{B} - \overset{+}{\underset{\underset{X}{|}}{O}}\text{-}H \qquad (3)$$



$$F_3\overset{-}{B} - \overset{+}{\underset{\underset{X}{|}}{O}}\text{-}H + CH_2{=}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} = F_3\overset{-}{B} - \underset{\underset{X}{|}}{O} + CH_3\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}} \qquad (4)$$

Where X may be H, $(CH_3)_3C$, or CH_3COO.

In Figure 9, the molecules involved in such a proton transfer are shown pictorially for isobutene and $F_3B.OH_2$ complex. Figure 9B shows the F_3BOH_2 complex. The structure of this compound has not been determined; the valence angles and bond distances which we have used have been taken by analogy with the structure reported for the dimethyl ether-boron trifluoride complex (11). The van der Waals' radii of the atoms have been taken as: O, 1.4; F, 1.35; H, 1.2. These are the normal values given by Pauling (12). The van der Waals' radius for boron has been taken to be 0.8A greater than the covalent raius according to the general rule suggested by Pauling. Figure 9A shows the isobutene molecule, and Figure 9C shows the carbonium ion $(CH_3)_3C^+$.

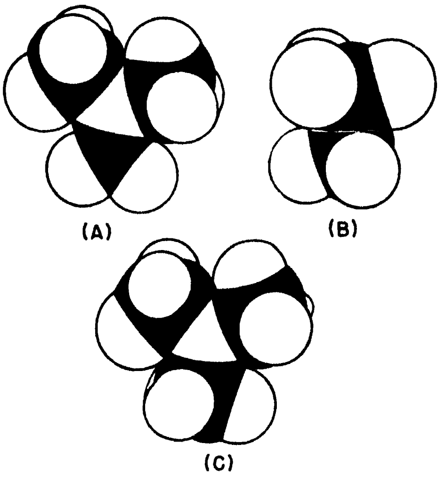


Fig. 9. Models of (A) $CH_2{=}C(CH_3)_2$, (B) F_3BOH_2, and (C) $(CH_3)_3C^+$.

The transfer of a proton from the $F_3B.OH_2$ complex to the planar isobutene molecule will lead to a planar $(CH_3)_3C^+$ carbonium ion. After the proton is transferred from the oxygen of $F_3B\ OH_2$ to the CH_2 group of $CH_2{=}C(CH_3)_2$, the positive charge which develops on the central tertiary carbon atom of $(CH_3)_3C^+$ will be attracted to the negative charge on the boron. This coulombic attraction which results from the transfer of a proton from the one molecule to the other is about 80 kcal. in magnitude, and will be an important factor in promoting this proton transfer.

It is difficult to assess the energetics of this proton transfer because one requires a knowledge of the electron affinity of the F_3BOH

radical. Since complexes of the type F_3BOH_2 have been found to be very strong acids (5), it is evident that the coordinate link between the oxygen and the boron causes a marked increase in electron affinity from OH to F_3BOH, and it is this term that will be the important one in any such calculation.

In discussing the possibility of this proton transfer we may consider the compound $BF_3.2H_2O$. According to Klinkenberg and Ketalaar (13), the solid $BF_3.2H_2O$ is a hydronium salt of the monohydroxylfluoboric acid, H (BF_3OH), and has the structure OH_3^+ $(BF_3OH)^-$. This indicates that the transfer of a proton can take place from $BF_3.H_2O$ to H_2O. Since the proton affinity of isobutene, estimated as about 189 kcal. (3b), is of the same order as that of water, given as 182 kcal. (14), it is quite reasonable to assume that the energetics involved in the transfer of a proton from F_3BOH_2 to isobutene are somewhat similar to those for the transfer of a proton from F_3BOH_2 to water.

Since diethyl ether behaves as a weak co-catalyst for the room temperature reaction, one must assume, according to the carbonium ion mechanism, that an ethyl positive ion is transferred from the $BF_3(OC_2H_5)_2$ catalyst to the olefin.

Propagation of Reaction

Because of the coulombic attraction between the $F_3\bar{B}OX$ residue and the positively charged carbon of the carbonium ion the propagation of the reaction under the conditions of our experiments probably occurs in such a way that the positive carbon always remains in contact with the $F_3\bar{B}OX$ residue. In this case the addition of a new monomer molecule will occur at the point of attraction of $F_3\bar{B}OX$ and the positive carbon of the carbonium ion. Even if the reaction occurs in solution with the polymer as solvent (a possibility which was mentioned earlier) it is very unlikely that dissociation of this ionic complex would occur in such a solvent.

Termination of Reaction

According to the carbonium ion mechanism, termination of the reaction cannot occur by mutual termination between positive carbon atoms. Termination can be brought about in two ways. One possibility is by the addition of a base to the positively charged carbon of the carbonium ion. In the presence of so strong an acid as boron trifluoride it is inconceivable that there can be any base present other than the $F_3\bar{B}OX$ residue, and termination by base addition could mean only the addition of this residue to the positive carbon atom.

To decide whether this mechanism is correct we may consider the results obtained for the slow reaction of isobutene. We have discussed earlier the fact that, in these experiments, one water molecule produces at least 2000 polymer molecules. This fact eliminates, in this case, the possibility of terminating the reaction by the addition of the catalyst residue $F_3\bar{B}OX$ to the carbonium ion.

Another possible method of termination is by the loss of a proton from a CH_3 or CH_2 group adjacent to the positive carbon atom, with the formation of a carbon-carbon double bond. This proton could be lost in two ways. It might be lost to a monomer molecule to give a carbonium ion which could thus attack another monomer. (R. L.

Meier, private communication, has also postulated the occurrence of this process in the polymerization of 2-butene by aluminium chloride.) Alternatively it could be lost to the $F_3\bar{B}OH$ residue, thus regenerating the original $F_3B \leftarrow O <^{H}_{X}$ complex which would then be available for the initiation of further reaction. (Similar methods of termination have been put forward in connection with the titanium tetra-chloride catalyzed reaction (3e).)

As discussed above, it is most probable that in our experiments the positive carbon is always in contact with the $F_3\bar{B}OX$ residue. In this case, proton transfer directly from a carbonium ion to a monomer molecule in the presence of the $F_3\bar{B}OX$ residue is thus little different from the transfer of a proton from the carbonium ion to the $F_3\bar{B}OX$ residue and the further transfer of that proton to a monomer molecule.

Steric Hindrance in the Polymer

The termination mechanism postulated in the preceding section would lead to the formation of a product which is a monoolefin with the double bond in the 1 or 2 position. The double bond may of course have been eliminated by the cyclization of the olefin, but we consider this to be extremely improbable. Since the polymer obtained at room temperature by the technique described in this paper is a mobile liquid of molecular weight corresponding to about five monomer units, it is of interest to discuss the question as to whether low-molecular olefins of this type would be expected to polymerize further. Chalmers (15) has shown that the production of long-chain polymers will occur only if the end of the growing polymer chain is active and will react with monomer molecules faster than two monomer molecules will react with each other. Once a growing polymer molecule has been terminated by the loss of a proton the molecule has lost this activity and will then react further only if it is attacked by an active molecule or if it is reactivated. Union between two such polymers will result in a molecule for which further growth is prevented by steric hindrance. This is found to be the case for di-isobutene; the action of boron trifluoride on this liquid produces practically no polymer of greater molecular weight than $C_{16}H_{32}$ (9). This we believe, is due to the fact that since already in polyisobutene the methyl groups of one isobutene unit are appreciably compressed against those of the adjacent unit, it would be sterically impossible to replace one methyl group in each isobutene unit by a neopentyl group, $(CH_3)_3CCH_2$, to give a long-chain polymer made up of di-isobutene units (9,16).

The above discussion would lead us to expect that the double bond in the polymer molecule is in such a position that absorption of bromine by the polymer would be sterically hindered. It is of interest, therefore, that we find that the product of this polymerization reaction absorbs bromine much more slowly than does di-isobutene. Further, whereas 25% of the absorption of bromine by di-isobutene is due to addition, in the case of the product of our polymerization experiments none of the bromine taken up is absorbed by straight addition.

Acknowledgment

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Synopsis

The polymerization reaction which occurs when butene vapor is mixed with boron trifluoride gas has been studied under various conditions. It has been found that this polymerization occurs only if a third component, or cocatalyst, is present. The function of the cocatalyst has been investigated, and the mechanism of the polymerization reaction is discussed.

Résumé

La réaction de polymérisation du butène, à l'état gazeux, additionné de trifluorure de bore, a été étudiée dans diverses conditions. Cette polymérisation ne se produit qu'en présence d'un troisième composant, jouant le rôle d'un cocatalyseur. Le rôle de ce dernier a été examiné, et le mécanisme de la réaction de polymérisation est discuté.

Zusammenfassung

Die Polymerisation die stattfindet, wenn gasförmiges Butylen mit Bortrifluorid gemischt wird, wurde unter verschiedenen Verhältnissen untersucht. Es wurde gefunden dass diese Polymerisation nur stattfindet, wenn ein dritter Stoff, oder Mitkatalysator, anwesend ist. Die Funktion des Mitkatalysators wurde untersucht und der Mechanismus der Polymerisation wird erörtert.

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Redox Recipes. I. Reaction between Ferrous Iron and Peroxides. General Considerations *

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INTRODUCTION

The reaction between ferrous iron and peroxides, particularly hydrogen peroxide, is of considerable importance in many fields and has been studied from several points of view. The usefulness of this reaction in organic chemistry was first recognized by Fenton (13), in the preparation of dihydroxymaleic acid, and by Ruff (43), in the degradation of sugars. Ferrous iron has been widely used as a reagent in analytical chemistry for the determination of organic peroxides, particularly hydroperoxides, although it has frequently been found that the reaction between ferrous iron and hydroperoxides is not stoichiometric (6,31,33). The polymerization of vinyl monomers can be initiated by the ferrous iron-hydrogen peroxide reaction. Recently it has been found (37,47,49) that polymerizations initiated by the reaction between ferrous iron and organic peroxides or hydroperoxides are of considerable practical importance in the so-called redox polymerizations (v.i.). An understanding of the mechanism of the reaction between ferrous iron on the one hand and hydrogen peroxide, organic peroxides, and hydroperoxides, on the other, is essential for an understanding of the mechanism of redox polymerization systems. In the present paper the mechanism of the former types of reactions is reviewed; in subsequent papers results obtained with various types of redox emulsion polymerization recipes will be presented.

In biochemistry the reaction of iron with hydrogen peroxide is of particular importance, inasmuch as atmospheric oxygen frequently reacts through hydrogen peroxide as an intermediate, while the action of many enzymes is believed to resemble that of ferrous iron (48); accordingly we find that the proposed mechanism of the ferrous iron-hydrogen peroxide reaction which is most widely accepted at present (that of Haber and Weiss (20)) was developed as an extension of a mechanism advanced for the action of enzymes on hydrogen peroxide, by Haber and Willstätter (21). In the mechanism of Haber and Weiss it is proposed that a hydroxyl radical is formed in the initial step of the reaction. This radical has very strong dehydrogenating properties and is extremely reactive. Accordingly, it may be stated that the wide importance of the ferrous iron-hydrogen peroxide reaction is due to the formation of a highly active substance (such as hydroxyl radical) from the reaction of two common and relatively stable compounds.

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SURVEY OF MECHANISMS PROPOSED FOR THE FERROUS IRON-HYDROGEN PEROXIDE REACTION

The mechanism of the reaction between ferrous iron and hydrogen peroxide has been studied much more extensively than those of the reactions between ferrous iron and other peroxides, for which, however, mechanisms may be inferred on the basis of that adopted for the former reaction. While an exact study of the kinetics of the ferrous iron-hydrogen peroxide reaction has been carried out only recently (12), several characteristic features of this reaction have been known since the beginning of the present century. These features, which the various proposed mechanisms have attempted to explain, may be summarized as follows.

1. In aqueous solutions containing only ferrous iron, hydrogen peroxide, and stable inorganic salts and acids, the stoichiometric equation:

$$H_2O_2 + 2Fe^{++} + 2H^{+} = 2Fe^{+++} + 2H_2O \qquad (1)$$

is obeyed when ferrous iron is present in excess over the peroxide. 2. When the peroxide is in large excess over the ferrous iron, less ferrous iron is oxidized than would correspond by equation 1 to the hydrogen peroxide consumed. The remaining hydrogen peroxide is decomposed to oxygen and water. 3. In the presence of many organic compounds, as well as of certain easily oxidized inorganic compounds such as iodide ion, part of the hydrogen peroxide oxidizes the added compounds (which may be termed "acceptors").

The decomposition of hydrogen peroxide to water and oxygen may be regarded formally as oxidation of one molecule of hydrogen peroxide by another:

$$H_2O_2 + H_2O_2 = 2H_2O + O_2 \qquad (2)$$

Thus this reaction is formally similar to the reaction between hydrogen peroxide and various organic compounds. Since these reactions are accelerated by, or occur only in company with, the reaction between hydrogen peroxide and ferrous iron, the former reactions are said to be induced by the latter reaction, following the customary phenomenological terminology (28). The induced oxidation of organic compounds is treated in detail in a subsequent section and will be mentioned in this section only insofar as it relates to the mechanism of the reaction between ferrous iron and hydrogen peroxide in pure aqueous solution.

The proposals which have been put forth to account for the induced oxidation of organic compounds or of hydrogen peroxide may be grouped in four classes: 1. activation of the "acceptor" by formation of a complex with ferrous iron (52); 2. intermediate steps of high energy (29); 3. formation of higher oxides of iron (9,35); 4. formation of other highly active intermediate compounds (20,41). The first of these concepts, advanced by Wieland to account for the induced oxidation of tartaric acid and similar compounds, was disproved by Goldschmidt and Pauncz (19), who showed by measurements of absorption spectra that no complex is formed in acid solution between ferrous iron and glycollic acid, and that ethanol, which certainly forms no complex, can be oxidized by the combination of ferrous iron and hydrogen peroxide. The view that reactions liberate energy (as for example, radiant energy) which can then activate other processes, was at one time widely held, but is, in general, no longer regarded as correct.

Manchot proposed (36) that the ferrous iron-hydrogen peroxide reaction proceeds through higher valence states of iron, either tetravalent or pentavalent; this appears to have been the first mechanism proposed for this reaction. In a later paper (35) Manchot reported that when ferrous iron is added slowly to very dilute solutions of hydrogen peroxide, 1.5 moles of hydrogen peroxide are consumed per mole of ferrous iron, while higher values are found in more concentrated solutions of peroxide. To account for these results, a mechanism was described in which the first step is the formation of pentavalent iron:

$$2FeSO_4 + 3H_2O_2 = Fe_2O_5 + 2H_2SO_4 + H_2O \qquad (3)$$

However, it was shown subsequently by Haber and Weiss (20) that when the iron and peroxide solutions are mixed together much more efficiently then was done by Manchot and Lehmann, reaction ratios much higher than 1.5 may be found, even in very dilute solutions; the experimental basis for the mechanism of Manchot was thus disproved. Furthermore, Baxendale, Evans, and Park (2) have found that the reaction between hydrogen peroxide and ferrous iron is first order in each of the reactants, when a rate constant of 62 liters mole^{-1} sec.$^{-1}$ at 25°; these kinetics would not follow from a reaction according to equation 3. The evidence against the mechanism of Manchot appears conclusive.

The formation of tetravalent iron was proposed by Bray and Gorin (9) in connection with the ferric iron-catalyzed decomposition of hydrogen peroxide (v.i.). The steps which are pertinent to the reaction between ferrous iron and hydrogen peroxide are the following:

$$Fe^{++} + H_2O_2 = FeO^{++} + H_2O \qquad (4)$$

$$FeO^{++} + H_2O_2 = Fe^{++} + H_2O + O_2 \qquad (5)$$

and the reverse of the disproportionation reaction:

$$2Fe^{+++} + H_2O = Fe^{++} + FeO^{++} + 2H^{+} \qquad (6)$$

Step 4 is the initiation step; steps 4 and 5 form a chain reaction, with ferrous iron and ferryl iron (FeO^{++}) as chain carriers; and the reverse of step 6 is the termination step. It is interesting that in this mechanism, the initiation step is also a propagation step.

The mechanism proposed by Haber and Weiss (20) for the induced decomposition of H_2O_2 by ferrous iron is the following:

$$Fe^{++} + H_2O_2 = Fe^{+++} + OH^{-} + HO\cdot \qquad (7)$$

$$HO\cdot + H_2O_2 = H_2O + HO_2\cdot \qquad (8)$$

$$HO_2\cdot + H_2O_2 = O_2 + H_2O + HO\cdot \qquad (9)$$

$$HO\cdot + Fe^{++} = Fe^{+++} + OH^{-} \qquad (10)$$

Reaction 7 is the initiation step of the chain reaction, in which the HO· free radicals are produced; equations 8 and 9, which are the original Haber-Willstätter equations (21), represent the propagation reaction; and equation 10 is the termination step. As shown in the following section, it is permissible to replace step 9 with another step, equation 18, involving reaction between ferric iron and perhydroxyl radical.

The initial steps of the reaction according to the mechanisms of Haber and Weiss and of Bray and Gorin are formally somewhat similar. Both mechanisms lead to the same kinetics, and to the same expression for the reaction ratio (established experimentally by Haber and Weiss (19,20):

$$\frac{d(H_2O_2)}{d(Fe^{++})} = 0.5 + \frac{k_a(H_2O_2)}{k_b(Fe^{++})} \qquad (11)$$

where k_a and k_b may represent the rate constants for step 5 and the reverse of step 6, respectively, or for steps 8 and 10, respectively, dependent on the type of the mechanism chosen. Values reported (20) for the ratio k_8/k_{10} are in the neighborhood of 0.02, depending somewhat on the acidity. The ferryl ion may be regarded as an oxide of tetravalent iron, or alternatively, as a compound of trivalent iron with univalent oxygen, just as the hydroxyl radical may be regarded as a compound of a hydrogen ion with a univalent oxygen atom; accordingly, both the ferryl ion and the hydroxyl radical should react readily with acceptors. It is of interest that formation of a compound which may be regarded as an intermediate in the formation of either ferryl iron or the hydroxyl radical, was proposed by Mummery (41) in 1913; this hypothetical compound was designated as "ferrous perhydrol," $\mathrm{Fe}{<}^{\mathrm{SO_4H}}_{\mathrm{OOH}}$, but was not isolated.

The following observations may be cited in support of the free-radical mechanism as opposed to that involving tetravalent iron. First, the hydroxyl (HO·) and perhydroxyl (HO_2·) free radicals have been assumed to exist on the basis of kinetic studies of other systems (e.g., the hydrogen peroxide-ozone system studied by Taube and Bray (45)); on the other hand, the existence of the ferryl ion has not been found necessary to explain the data found with any other system (18,22). Second, in a study by the authors of the induced reaction between hydrogen peroxide and ethanol, in which ethanol competes with ferrous iron for the active intermediates, no salt effect was found, indicating that the active intermediate is uncharged; these results will be presented in more detail elsewhere.

FERRIC IRON-CATALYZED DECOMPOSITION OF HYDROGEN PEROXIDE

It has been known for some time that hydrogen peroxide is catalytically decomposed in the presence of ferric iron. The simple rate law:

$$-\frac{d(H_2O_2)}{dt} = k\,(H_2O_2)\,\frac{(Fe^{+++})}{(H^+)} \qquad (12)$$

was first presented by von Bertalan (4), on the basis of experiments carried out in solutions of sufficient acidity (0.001 to 0.1 *M* in sulfuric acid) to prevent the formation of colloidal hydrous ferric oxide; possible complications arising from the partial hydrolysis of ferric iron (32) were not considered. von Bertalan obtained a value of 0.07 for k at 40°, with a temperature coefficient of 3.25 per 10°, concentrations being expressed in moles/liter, and time in minutes. Confirmation of this rate law was reported by Bray (8), who gave a value of 0.125 for k at 40° (9). Bray noted (8) that the rate law (equation 12) holds with concentrations of hydrogen peroxide greater than 0.02 *M*, but that "at lower concentrations the value of k decreased gradually during each run."

In a recent article by Andersen (1b) it is shown experimentally that the rate of the ferric iron-catalyzed decomposition of hydrogen peroxide is not represented correctly by equation 12 but by a more complicated expression:

$$-\frac{dt}{d(H_2O_2)} = \frac{0.4343}{B(H_2O_2)} + \frac{A}{B(H_2O_2)^2} \qquad (12a)$$

The values of the constants A and B, given below, are such that, as a first approximation, expression 12a reduces to equation 12; at a pH of 2 or less, expression 12a may be regarded as equivalent to equation 12 with a small correction term. The experimental conditions used by Andersen were similar to those employed by von Bertalan, except for the use of nitric acid (by Andersen) rather than the more strongly complexing sulfuric acid. The range of concentrations of acid and of ferric iron used by Andersen were 0.01-0.04 *M*, and 0.001-0.004 *M*, respectively. It is to be expected that the small correction term, which on the basis of the experimental data of Andersen constitutes the chief difference between expressions 12 and 12a, could be derived on the basis of various mechanisms by introduction of various side reactions; however, a detailed examination of the possible reactions is beyond the scope of this paper.

In many of the mechanisms which have been proposed for the catalytic decomposition of hydrogen peroxide, the intermediate formation of ferrous iron is assumed; in other mechanisms, which are considered first below, this assumption is not made.

A mechanism not involving the formation of ferrous iron was proposed by Bohnson and Robertson (5), who concluded from measurements of absorption spectra that the ferrate ion, FeO_4^{--}, was formed in mixtures of hydrogen peroxide and ferric chloride. The pH of these mixtures was not stated; it is, of course, known that ferrate compounds are stable only in strongly alkaline medium. Consequently, it is uncertain whether their mechanism, given below, is of any significance with respect to the reaction in acid solutions, such as must normally be used to prevent the formation of colloidal hydrous ferric oxide.

$$3H_2O_2 + 2Fe^{+++} + 2H_2O = 2FeO_4^{--} + 10H^+ \qquad (13)$$

$$2FeO_4^{--} + 3H_2O_2 + 10H^+ = 2Fe^{+++} + 3O_2 + 8H_2O \qquad (14)$$

or:

$$2FeO_4^{--} + 2H_2O_2 + 8H^+ = 2Fe^{++} + 3O_2 + 6H_2O \qquad (14a)$$

Andersen finds (1b) that the rate law 12a, established by his experiments, can be derived from the following mechanism, not involving the formation of ferrous iron:

$$Fe^{+++} + HO_2^- = FeOH^{++} + [O] \qquad (15)$$

$$[O] + HO_2^- = OH^- + O_2 \qquad (16)$$

where step 15 is reversible. The dependence of the constants A and B upon concentrations of reactants and of hydrogen-ion is calculated on the basis of this mechanism to be as follows: B is proportional to the term:

$$\frac{K_a}{K_h + (H^+)} \; (Fe^{+++})_{total}$$

and A is proportional to the term:

$$\frac{K_h}{K_a} \times \frac{(H^+)}{K_h + (H^+)} \; (Fe^{+++})_{total}$$

where K_a is the acid constant of hydrogen peroxide, and K_h is the first hydrolysis constant of ferric iron (equation 21, below). The experimental data of Andersen are in good agreement with the calculated constants, using the value of 2.5×10^{-3} for K_h, established by Lamb and Jacques (32).

With regard to the mechanism proposed by Andersen, it should be pointed out, first, that step 15 has a positive standard free energy of 18,000 cal., based on the above value of K_h, and data given by Latimer ("Oxidation Potentials," 1938) for the decomposition of oxygen and the perhydroxide ion; and, second, that because the active form of hydrogen peroxide in both equations 15 and 16 is the perhydroxide ion, which is present in very low concentrations (since $K_a = 2.4 \times 10^{-12}$), an unusually high rate constant (10^{10} liters mole^{-1} min.$^{-1}$) is found for the forward step 15. Unless the entropy term in the expression for the free energy of step 15 is extremely large, the combination of a positive free energy with a high rate constant appears improbable.

Mechanisms in which ferrous iron is assumed as an intermediate are of more direct bearing upon the ferrous iron-hydrogen peroxide reaction, which is the principal subject of the present paper. It has not proved possible to demonstrate experimentally that ferrous iron is formed in the course of the ferric iron-catalyzed decomposition of hydrogen peroxide. Manchot and Wilhelms (36) tested for ferrous iron with ferricyanide in a mixture of hydrogen peroxide and ferric iron; however, as pointed out by Mummery (41), ferricyanide is reduced by hydrogen peroxide to form ferrocyanide, which would precipitate with ferric iron. Attempts to detect ferrous iron with o-phenanthroline or α, α'-dipyridyl have shown (29) that the concentration of ferrous iron in the solution before addition of the complexing agent is below the limit of sensitivity of the test, since the color of the complex is not formed immediately upon addition of the complexing agent, but develops slowly. As discussed below, the reactions which occur in mixtures of ferric iron, hydrogen peroxide, and o-phenanthroline or α, α'-dipyridyl, are poorly understood and are subject to contrary interpretations (20,35).

The mechanisms of greatest important are those of Bray and Gorin (9) and of Haber and Weiss (20). Bray and Gorin assume that ferric and ferrous iron are in rapid and reversible equilibrium according to equation 6. The ferrous iron thus formed in low concentration from ferric iron reacts according to equation 4, which is the rate-determining step; oxygen is formed by step 5. The rate law (equation 12) is readily derived on this basis.

Haber and Weiss, in order to arrive at the rate law (equation 12), take as the primary and rate-determining step the reaction:

$$Fe^{+++} + HO_2^- = Fe^{++} + HO_2 \qquad (17)$$

where the concentration of HO_2^- would be equal to $K_a(H_2O_2)/(H^+)$. The perhydroxyl radical can be consumed in three ways: by the reverse of step 17 (denoted as 17r), by step 9, or by reaction with ferric iron:

$$Fe^{+++} + HO_2\cdot = Fe^{++} + O_2 + H^+ \qquad (18)$$

Normally the reaction is stated to proceed through steps 17 and 18, from which the rate law (equation 12) can be derived, if it is assumed that the ferrous iron formed in these two steps is consumed by steps 7 and 10, and that step 7 does not initiate the chain reaction 8 and 9. Indeed, if it is assumed that step 8 does not occur, then step 18, which was introduced by Haber and Weiss, need not be considered; note that step 18 followed by step 7 is equivalent to step 9. Accordingly, we find that consideration of the three steps 17, 9, and 10 (neglecting 17r) leads directly to the rate law (equation 12).

In like manner, the reaction between ferrous iron and hydrogen peroxide can be treated equally well on the basis of steps 7, 8, 18, and 10, or of the original Haber-Weiss steps, 7, 8, 9, and 10; both schemes lead to expression 11 for the reaction ratio. There is, then, no kinetic basis for choice between steps 9 and 18; but it is an unnecessary complication to adopt one of these steps in considering the reaction with ferrous iron, and the other, with ferric iron; it appears simpler to use the same step throughout.

It is of special significance to realize that the conditions of the ferric iron-catalyzed decomposition are precisely those under which, according to the results found for the reaction between ferrous iron and hydrogen peroxide, chain decomposition through steps 8 and 9 should take place; namely, concentration of hydrogen peroxide much greater than that of ferrous iron.

Under these conditions, hydroxyl radicals, formed according to step 7 or step 9, should react with hydrogen peroxide (step 8) rather than with ferrous iron (step 10). We have examined the kinetics to be expected on the basis of various groups of steps. Consideration of the six equations 7, 8, 10, 17, 17r, and either 9 or 18, leads to very complicated expressions. Simplification of these expressions, by neglecting various steps in comparison with other competing steps, in no case leads to expressions of the form of equations 12 or 12a; in most of these limiting cases, the predicted rate of disappearance of hydrogen peroxide is proportional to the concentration of hydrogen peroxide raised to some power greater than one. An expression in the first power of this concentration results from consideration of equations 7, 8, 10, 17, 17r, and 18, with the assumption that the rates of steps 10 and 17r are small; this expression is:

$$\frac{d(H_2O_2)}{dt} = 2k_7(H_2O_2)(Fe^{+++})\left(\frac{K_a k_{18} k_{17}}{k_7 k_{17r}(H^+)}\right)^{1/2} = k_{19}\frac{(H_2O_2)(Fe^{+++})}{(H^+)^{1/2}} \qquad (19)$$

Expression 19 differs from 12 only in the concentration of hydrogen ion. If step 17 is replaced by:

$$FeOH^{++} + HO_2^{-} = Fe^{++} + HO_2\cdot + OH^{-} \tag{20}$$

where the concentration of $FeOH^{++}$ is determined by the rapidly established hydrolysis equilibrium (32):

$$(FeOH^{++}) = K_h \frac{(Fe^{+++})}{(H^{+})} \tag{21}$$

we find that consideration of equations 7, 8, 10, 20, 17r, and 18, with the assumption that the rates of steps 10 and 17r are small (specifically, small in comparison to the rates of steps 8 and 18, respectively), leads to the following expression:

$$\frac{d(H_2O_2)}{dt} = 2\left(\frac{k_7 k_{18} k_{20}\, K_a K_h}{k_{17r}}\right)^{1/2} \frac{(H_2O_2)\,(Fe^{+++})_{total}}{K_h + H^{+}}$$

$$= k_{22} \frac{(H_2O_2)(Fe^{+++})_{total}}{K_h + H^{+}} \tag{22}$$

Note that in order to derive expression 22 it must be assumed that ferrous iron and perhydroxyl radical react according to equation 17r rather than the reverse of step 20; this assumption is justified, since the reverse of step 20 would be a third-order reaction including the hydroxide ion (present in very low concentration in acid solution) as a reactant.

The assumptions which are made in deriving equation 22 are equivalent to assuming that decomposition of hydrogen peroxide proceeds chiefly through the cycle of steps 7, 8, and 18, the role of step 20 being simply to replenish the ferrous iron and perhydroxyl radical consumed by the side reactions 17r and 10. Thus the reaction between ferrous iron and hydrogen peroxide, rather than being suppressed as was done in the original Haber-Weiss treatment of the ferric iron-catalyzed decomposition of hydrogen peroxide, is found to be of primary importance in bringing about this catalytic decomposition.

The dependence upon hydrogen-ion concentration of the rate of decomposition of hydrogen peroxide, given by equation 22, is identical with that given by the expression of Andersen, above, with the omission of the small correction term (the last term of equation 12a). At a pH of 2 or less, equation 22 reduces to the rate law of von Bertalan. Thus it is seen that a free radical mechanism can be devised which will account for the experimental observations in a more satisfactory manner than that given originally by Haber and Weiss (20).

In the original mechanism of Haber and Weiss for ferric iron catalysis, ferrous iron is believed to act as a chain-breaker, through step 17r; while in the free-radical mechanism given above, as well as in the mechanism of Bray and Gorin, ferrous iron is a chain-carrier. Thus a reduction in the steady-state concentration of ferrous iron would be expected to bring about an increased rate of catalytic decomposition, on the basis of the former mechanism, and a decreased rate, on the basis of the latter two mechanisms. Kuhn and Wassermann (29) studied the decomposition of hydrogen peroxide in the presence of ferric or ferrous iron, together with the strong complexing agents, α , α'-dipyridyl, and o-phenanthroline. The found that both the extent and the rate of the decomposition were exceptionally large when the iron and dipyridyl (or phenanthroline) were mixed in the presence of relatively concentrated hydrogen peroxide in acetate buffers of pH 4.1-5.3. This effect they termed "Katalasestoss."

It is clear that if, under the conditions used, ferrous iron reacts much more rapidly with hydrogen peroxide than it does to form the orange or red complex, then the steady-state concentration of ferrous iron will not be appreciably diminished by formation of this complex. Kuhn and Wassermann reported that ferrous iron, when added to a mixture of hydrogen peroxide and dipyridyl or phenanthroline, in acetate buffer, was immediately oxidized to ferric iron, which was then slowly reduced (by hydrogen peroxide) to yield the orange or red ferrous complex. We have carried out some experiments to check this point, and have found that under typical conditions used by Kuhn and Wassermann, the addition of ferrous iron (0.0005 *M*) to a rapidly stirred mixture of hydrogen peroxide (0.645 *N*) and o-phenanthroline (0.0025 *M*). in an acetate buffer of pH 4.1, led to the immediate formation of an orange color, but that this color corresponded to the complexing of only one-sixth of the amount of ferrous iron added. Dipyridyl, which has been shown (3, 19) to form the ternary complex with ferrous iron with roughly one ten-thousandth the velocity of phenanthroline, might be expected to give no red color at all under these conditions. Actually we have found that some red color was developed immediately when dipyridyl was used in place of phenanthroline in the above experiment, but that this color corresponded to complexing of only one-fifteenth of the amount of ferrous iron added. In any case it appears that the steady-state concentration of ferrous iron would not be appreciably diminished by formation of the stable orange or red complex, under the conditions of the "Katalasestoss."

On the other hand, it is known (3,19) that both the mono- and di-phenanthroline (or dipyridyl) complexes of ferrous iron are formed much more rapidly than are the ternary complexes. Thus it is likely that the steady-state concentration of ferrous iron in the ferric iron-hydrogen peroxide system, will be lowered by the addition of dipyridyl or phenanthroline, as a result of formation of these partially completed complexes. But these complexes, in which the ferrous iron is not completely shielded, may react with hydrogen peroxide; indeed, Kuhn and Wassermann suggested that these complexes behaved similarly to the enzyme catalase. Thus the experiments of Kuhn and Wassermann do not furnish any conclusive evidence regarding the mechanism of the peroxide-iron reaction. Further experiments of this nature are being carried out by Baxendale and George, as mentioned in reference (3), and should aid in our understanding of the mechanism.

There remains to be considered the mechanism of von Bertalan (4), which was proposed again in a recent preliminary publication by Abel (1a). von Bertalan showed that the rate law, 12, would follow if the rate-determining step were first order in ferric iron and perhydroxide ion, HO_2^-; however, no postulate was made concerning the products formed in such a step. The over-all reaction was believed by von Bertalan to consist of the following two steps:

$$2Fe^{+++} + H_2O_2 = 2Fe^{++} + 2H^+ + O_2 \qquad (23)$$

$$2Fe^{++} + 2H^+ + H_2O_2 = 2Fe^{+++} + 2H_2O \qquad (1)$$

The standard E.M.F. values of the two cells represented by equations 23 and 1 are 0.09 volt and 1.00 volt, respectively, so that both over-all reactions can proceed as written.

The over-all reactions 23 and 1 were suggested by Abel (1a), who pointed out the analogy between these steps and those by means of which he has accounted for the catalytic action of halides in the decomposition of hydrogen peroxide. However, it is obvious that the same objection which was made earlier to the original mechanism of Haber and Weiss applies equally to the mechanism of von Bertalan, or of Abel: that the reaction between ferrous iron and hydrogen peroxide does not proceed stoichiometrically (equation 1) when hydrogen peroxide is present in much higher concentration than ferrous iron. The induced decomposition of hydrogen peroxide, brought about by the reaction between hydrogen peroxide and ferrous iron, must be taken into account in any mechanism for ferric iron catalysis in which the formation of ferrous iron is assumed.

THE FENTON REACTION

The oxidation of an organic compound by hydrogen peroxide in the presence of an iron salt is termed here a Fenton reaction. A number of compounds which ordinarily are attacked very slowly, if at all, by hydrogen peroxide, are readily oxidized by the Fenton reagent (the combination of hydrogen peroxide and ferrous iron). This reaction was first described in 1894 by H. J. H. Fenton (13), who reported that upon treatment with any of several oxidizing agents, in the presence of a trace of ferrous iron, tartaric acid is oxidized to dihydroxymaleic acid. Suitable oxidizing agents include chlorine water, hypochlorous acid, potassium permanganate, or preferably hydrogen peroxide. A violet color is formed in the Fenton oxidation of tartaric acid, as was first noticed in 1876 by Fenton (12). The oxidation of compounds other than tartaric acid by hydrogen peroxide in the presence of ferrous iron was also attempted by Fenton. The reaction was found to proceed satisfactorily with glycollic aldehyde (14), various sugars (14), and a number of polyhydric alcohols, including glycerol (15).

There has been some controversy among the early workers as to whether the oxidation of various acceptors by hydrogen peroxide, which is found in the presence of ferrous iron, can also take place if ferric iron is used in place of ferrous iron. It has been established by Goldschmidt and co-workers (16,17) that the presence of ferrous iron is required for these oxidations, and that ferric iron is active only if it is reduced by the acceptors or their oxidation products. Accordingly the Fenton reaction may be described as the oxidation of an organic compound by hydrogen peroxide, induced by the reaction between ferrous iron and hydrogen peroxide.

Wieland and Franke (52) carried out an extensive study of the Fenton reaction with various substrata, including formic aicd, and glycollic acid and a number of other hydroxy acids. As mentioned in a previous section, their proposed mechanism, involving formation of a complex between ferrous iron and the substratum, was disproved by Goldschmidt and Pauncz (17). The induced oxidation of formic acid was studied earlier by Mummery (41). Kultyugin and Sokolova (30) have studied the oxidation of a number of alcohols and other compounds; however, only the formation of carbon dioxide was measured in this work. Carbon dioxide was formed from the oxidation of glycerol but not from monohydric alcohols.

Before considering the oxidation of more complicated compounds such as glycerol and various sugars, the mechanism of the oxidation of ethanol will be discussed. As shown in the previous sections, the initial step of the reaction between hydrogen peroxide and ferrous iron may lead to the formation of either ferryl iron or the hydroxyl radical. Either of these compounds would be expected to dehydrogenate ethanol. If this dehydrogenation does not occur at the weakest bond, the radical formed may rearrange so as to give the more stable radical; in either case, the hydroxyethyl radical would be formed:

$$FeO^{++} + CH_3CH_2OH = Fe^{+++} + CH_3\underset{\bullet}{C}HOH + OH^- \qquad (24)$$

$$HO\cdot + CH_3CH_2OH = H_2O + CH_3\underset{\bullet}{C}HOH \qquad (25)$$

The hydroxyethyl radical can react with hydrogen peroxide, either directly (equation 28) or through reaction with ferric iron (equation 26). The latter reaction is in accord with either the free radical or the ferryl iron mechanism. Reaction with ferrous iron is also possible. The significant reactions are:

$$Fe^{+++} + CH_2\underset{\bullet}{C}HOH = Fe^{++} + H^+ + CH_3CHO \qquad (26)$$

and:

$$CH_3\underset{\bullet}{C}HOH + Fe^{++} + H^+ = CH_3CH_2OH + Fe^{+++} \qquad (27)$$

In order for the Fenton reaction to occur, it is necessary that reaction 26 take place in preference to 27; i.e., that under the experimental conditions, the radical reduce ferric iron or hydrogen peroxide rather than oxidize ferrous iron. Steps 24, 26, and 4 form a chain reaction in which hydrogen peroxide oxidizes ethanol to acetaldehyde, with the ferryl ion as the active oxidizing agent and chain-carrier. Alternatively, steps 25, 26, and 7 form a chain reaction with hydroxyl radical as the active intermediate. It is possible that in place of steps 26 and 7 the direct reaction:

$$CH_3\underset{\bullet}{C}HOH + H_2O_2 = CH_3CH(OH)_2 + HO\cdot = CH_3CHO + H_2O + OH\cdot \qquad (28)$$

may take place. In any case, it is clear that the oxidation of one ferrous ion by one molecule of hydrogen peroxide can lead, by a chain mechanism, to the oxidation of a large number of molecules of ethanol.

Reaction of the organic radical with dissolved oxygen in the solution is possible, but should not be of importance in the relatively concentrated solutions in which the Fenton reaction is ordinarily carried out. Reaction of the organic radical with another radical (such as the hydroxyl radical) should be of minor importance due to the low concentrations of radicals. Cases in which reaction of the organic radical with ferrous iron, or with oxygen, may be of importance, are discussed in the following section.

In reaction 26 the product is acetaldehyde, further oxidation of which by analogous reactions would lead to acetic acid. Goldschmidt and Pauncz (17), working with 1 molar solutions of ethanol and hydrogen peroxide, and 0.1 *M* ferrous sulfate, at 0°, showed that both these products are formed, together with ferric iron and oxygen, the latter resulting from induced decomposition of the hydrogen peroxide occurring simultaneously with induced oxidation of the ethanol and acetaldehyde. In a typical experiment, in 0.2 *N* sulfuric acid, 41% of the hydrogen peroxide consumed went to form acetaldehyde; 41%, of acetic acid; 8% to form ferric iron; and 10% to oxygen. The extent of the Fenton reaction was much less in hydrochloric acid than in sulfuric acid; this is discussed in the following section. Experiments by the authors have shown that in solutions as dilute as 10^{-3} *M* in reactants, in the absence of oxygen, acetaldehyde is a product of the Fenton oxidation of ethanol.

The oxidation of glycerol by the Fenton reaction is of some practical importance, since, as shown by Fenton and Jackson (15), Witzeman (53), and den Otter (42), the primary oxidation product is glyceraldehyde, which is of physiological interest, and is difficult to synthesize in other ways; however, the purification of glyceraldehyde prepared in this way is difficult. The oxidation of glycerol to glyceraldehyde is, of course, exactly analogous to the oxidation of ethanol to acetaldehyde; but the subsequent reaction differs in that the oxidation products of glycerol reduce ferric iron, so that a relatively small amount of iron is sufficient to bring about considerable reaction. We have found that it is even possible to carry out this reaction with ferric rather than ferrous iron; although it is not certain whether the initial reaction is due to ferric iron, or to traces of ferrous iron or other impurities, the subsequent reaction must involve the reduction of ferric iron by the oxidation products of glycerol, since ferric iron cannot be used in the Fenton oxidation of ethanol. The products which have been found (42) in the Fenton oxidation of glycerol include glyceraldehyde, hydroxypyruvic aldehyde, methyl glyoxal, formaldehyde, formic acid, carbon dioxide, and oxalic acid.

The Fenton reaction is also of importance in sugar chemistry, Morrell and Crofts have shown (40) that various sugars are oxidized to the corresponding osones; that is, a hydroxyl group adjacent to the carbonyl group is oxidized to form another carbonyl group. Glucose, fructose, and sucrose all yield glucosone. Ruff (43) has found that various sugar acids are degraded by the Fenton reaction; thus, arabinose is formed from gluconic acid.

While only a few applications of the Fenton reaction have been given above, this reaction is of considerable importance and appears to warrant further study, in view of the more recent theoretical developments. Since the Fenton reaction frequently gives good yields of fairly strong reducing agents, such as glyceraldehyde or glucosone, it is sometimes stated (24) that the Fenton reagent is a mild oxidizing agent. Actually a very strong oxidizing or dehydrogenating agent (hydroxyl radical or ferryl ion) is formed in the Fenton reaction; the rate of formation of this strong oxidizing agent can be controlled, however, by adjusting the rate of addition of hydrogen peroxide to the mixture of the substratum with the iron salt, or by controlling the rate of reduction of the ferric iron (for example, by varying the temperature of the concentration of iron). The active oxidizing agent is present in very low concentration, and its dehydrogenating action is so strong that it may react with equal ease with both strong and weak reducing agents, depending on the rate of collision with the various substances present. Thus, in a mixture of glycerol and glyceraldehyde, the Fenton reagent will oxidize both compounds, while a weaker oxidizing agent would attack only the glyceraldehyde.

ANALYTICAL APPLICATIONS

Ferrous iron has been used extensively in the determination of organic peroxides of all types, particularly hydroperoxides. While the reaction between ferrous iron and hydrogen peroxide is not of major analytical significance, because of the number of other reagents available for the determination of hydrogen peroxide, study of the system with hydrogen peroxide affords valuable insight into the mechanism of the reaction with hydroperoxides, and will accordingly be taken up first.

As has been shown in the preceding sections, the reaction between ferrous iron and hydrogen peroxide can induce the decomposition of hydrogen peroxide, as well as the reaction between hydrogen peroxide and various organic compounds, if present. We have found that both effects may be of significance under typical analytical conditions. Thus, if it is attempted to determine 0.1 *N* hydrogen peroxide, in the absence of organic compounds, by the addition of an excess of ferrous iron, followed by titration of the unreacted ferrous iron, some error will result owing to the induced decomposition of the hydrogen peroxide which takes place during the early stages of the addition of ferrous iron, when the peroxide is present in large excess over the ferrous iron. If the ferrous iron is added from an ordinary pipet to a vigorously stirred solution of peroxide, we have found that approximately 1% of the hydrogen peroxide is decomposed in this way; the reverse mode of addition, as expected, does not lead to any error. If the ferrous iron is added very slowly, greater errors are found, as shown by other workers.

The determination of hydrogen peroxide by reaction with ferrous iron in the presence of many organic compounds, such as ethanol, is simply a Fenton reaction. We have found that in the absence of oxygen, the amount of hydrogen peroxide which reacts with ethanol may amount to more than 10 times that which reacts with ferrous iron. Not all organic compounds exhibit this behavior, however; for example, acetic acid and acetone lead to practically no induced reduction of hydrogen peroxide. Furthermore these latter compounds actually suppress the induced reaction between hydrogen peroxide and compounds such as ethanol; accordingly we may designate acetic acid and acetone as "suppressors", and ethanol, methanol, and acetaldehyde as "promoters." In a typical experiment, solutions in 1.5 *N* sulfuric acid of ferrous iron ($2 \times 10^{-3} M$), hydrogen peroxide ($5 \times 10^{-4} M$), and ethanol ($10^{-3} M$) were mixed together rapidly in the absence of oxygen; the molar reaction ratio of ferrous iron to hydrogen peroxide was 0.71 (compared with the stoichiometric value of 2.0). When the same experiment was repeated in the presence of 1 *M* acetic acid, in addition to the ethanol, the reaction ratio was 1.79; while with 10 *M* acetic acid in addition to the ethanol, the ratio was 1.95. It may be mentioned that chloride ion also behaves as a powerful suppressor; compare the decrease in extent of the Fenton reaction with ethanol found in the presence of hydrochloric acid, by Goldschmidt and Pauncz (previous section).

It appears that in a mixture containing both a suppressing and a promoting compound, these compounds compete for reaction with hydroxyl radicals (or ferryl ions). If a promoting compound reacts with the active oxidizing agent, a radical is formed which then reacts with hydrogen peroxide, according to step 26, resulting in induced reduction of the peroxide. If a suppressing compound reacts to form a free radical, then this radical must react with ferrous iron according to steps analogous to 27; thus the over-all reaction (sum of steps 7, 25, and 27) is the stoichiometric reaction between ferrous iron and hydrogen peroxide, according to equation 1, but proceeding through the intermediate formation of radicals derived from the suppressing compound. Independent evidence for the reaction of hydroxyl radicals with acetic acid and with chloride ion is furnished by the work of Taube and Bray (46).

The over-all course of the reaction in the presence of both suppressing and promoting compounds depends upon the relative extent to which these compounds react with hydroxyl radicals (or ferryl ions). It is of considerable analytical importance that the large deviations from the stoichiometric reaction which are found in the presence of small amounts of promoters may be, practically speaking, completely suppressed by the addition of a high concentration of a suppressor.

In the presence of oxygen, all the organic compounds which we have studied show qualitatively similar behavior, without distinction between "promoting" and "suppressing" compounds. The reaction between hydrogen peroxide and ferrous iron in the presence of oxygen and organic compounds leads to induced oxygen oxidation of ferrous iron. The extent of this oxidation may be quite high, particularly in very dilute solutions of peroxide and iron, in which the concentration of oxygen can be kept relatively high; depending on the experimental conditions, the amount of ferrous iron oxidized by the induced reaction may be two to three times as great as the amount oxidized by the stoichiometric reaction. On the other hand, in more concentrated solutions of ferrous iron and peroxide, in which the concentration of oxygen in air-saturated solutions is relatively low, induced reduction of the peroxide may equal or predominate over the induced oxygen oxidation of ferrous iron. It appears that the organic radical formed by dehydrogenation of an organic compound can add molecular oxygen, forming a peroxide radical, which can react with three ferrous ions, or can lead to autoxidation of the organic compound by a chain reaction. In contrast to the organic suppressors, chloride ion acts as a suppressor in the presence as well as in the absence of oxygen.

Turning to organic peroxides, some indication that the mechanism of the reaction between these compounds and ferrous iron is similar to that of the reaction between hydrogen peroxide and ferrous iron is afforded by the work of Wieland and Bossert (50), who showed that diethyl peroxide can be used in place of hydrogen peroxide in the Fenton oxidation of various compounds; that is, the reaction between these compounds and diethyl peroxide is induced by the reaction between diethyl peroxide and ferrous iron. Wieland and Chrometzka (51) showed that the reaction between ferrous iron and diethyl peroxide induces the decomposition, or disproportionation, of diethyl peroxide, to form ethanol and acetaldehyde.

We have studied in some detail the reaction between ferrous iron and cumene hydroperoxide (phenyldimethyl methyl hydroperoxide), which is a typical organic hydroperoxide and is farily soluble

(0.09 *M*) in water. The behavior of cumene hydroperoxide in its reaction with ferrous iron is qualitatively similar to the behavior of a mixture of hydrogen peroxide and an organic compound of the "promoting" type. Thus, the reaction between cumene hydroperoxide and ferrous iron in pure aqueous solution leads to considerable induced decomposition of the peroxide, in the absence of oxygen, and to considerable induced oxidation of ferrous iron, in the presence of oxygen. Addition of ethanol to the system increases the extent of both induced reactions; while addition of acetic acid suppresses the induced decomposition of peroxide in the absence of oxygen, but does not suppress the induced oxidation in the presence of oxygen. It is likely that the reaction between ferrous iron and an organic hydroperoxide, ROOH, proceeds in a manner similar to that of the reaction with hydrogen peroxide; for convenience, we may assume the formation of alkoxy radicals, RO·. The rates of reaction of these alkoxy radicals with the peroxide and with ferrous iron (steps corresponding to 8 and 10) may differ from the rates of steps 8 and 10, so that induced decomposition of the peroxide may take place even when ferrous iron is in excess over the peroxide, in the absence as well as the presence of added promoters.

The analysis of small quantities of hydroperoxides is of considerable importance, since hydroperoxides are generally formed initially in the autoxidation of many unsaturated organic compounds, including natural products such as fats (33), petroleum products (45) and rubber (7). While conflicting statements are found in the literature regarding the absolute accuracy of the ferrous methods under various conditions, in general it appears that many of the ferrous methods lead to high results (more peroxide found than actually present) when carried out in the presence of air, while low results are frequently found in the absence of air (31). The deviations in both directions may be of the order of several fold. Results which are fairly close to the true values have also been reported in many cases. These observations can be interpreted readily in the light of the considerations advanced above. Study of the fundamental principles underlying the reaction between ferrous iron and peroxides has also led us to the development of satisfactory procedures for the determination of hydroperoxides with ferrous iron. This work will be described in more detail in a subsequent publication. Evidence has been obtained in this laboratory that free radicals are formed in the interaction of persulfate and ferrous iron; this reaction is now being studied in greater detail.

INITIATION OF VINYL POLYMERIZATION

Within the last five years there has been a rapid development of the use of redox systems - that is, systems containing both an oxidizing and a reducing agent - for the initiation of vinyl polymerization. Polymerizations which are initiated by the reaction between an oxidizing and a reducing agent may be called redox polymerizations. The importance of polymerization recipes of this type was discovered by accident, at about the same time, in both England and Germany, in the following way. Polymerization of vinyl monomers is commonly initiated by oxidizing agents; in these polymerizations, oxygen is known to act as an inhibitor (27); accordingly various reducing agents were added to polymerization systems in order to remove gaseous oxygen; and it was discovered that not only were the induction periods eliminated, but in many cases the subsequent rates of polymerization were increased. Systematic study of the mechanisms of various redox recipes has been carried out by both English and German workers. The development of emulsion polymerization recipes of practical importance in Germany was of considerable interest to chemists in this country (28,49), and improved recipes for the production of synthetic rubber of the GR-S type have been developed subsequently in this country (47). Practical interest is attached to these recipes at present because they permit the production of synthetic rubber at low temperatures, thus obtaining a polymer of more desirable properties.

Initiation of polymerization by redox systems was first noticed in England by Bacon (1c), who termed this phenomenon "reduction activation." A systematic study was made of the rates of polymerization of various monomers, in aqueous solution, in the presence of various oxidizing and reducing agents. The oxidizing agents studied by Bacon included alkali persulfates, sodium hypochlorite, and ceric sulfate. A detailed study of the kinetics and mechanism of redox polymerization systems with persulfate as the oxidizing agent was carried out by Morgan (39). Both authors reported that initiation in the systems which they studied was much more effective with acrylonitrile and its derivatives than with butadiene and its derivatives, with styrene occupying an intermediate position. Further study of persulfate systems has been carried out by Bunn, Evans, and Baxendale (10).

Initiation of polymerization by means of the hydrogen peroxide-ferrous iron reaction was studied in detail by Baxendale, Evans, and Park (2), working in aqueous solution, and by Evans (11), working in aqueous solution in the presence of a detergent (trimethylcetylammonium bromide). These authors accepted the mechanism of Haber and Weiss, and in addition put forth the following steps:

$$\mathrm{HO\cdot + CH_2{=}CHX = HOCH_2\underset{\bullet}{C}HX} \qquad (29)$$

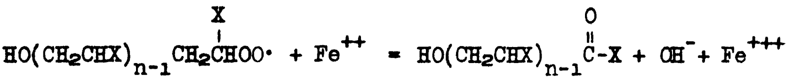
$$\mathrm{HOCH_2\underset{\bullet}{C}HX + nCH_2{=}CHX = (polymer)} \qquad (30)$$

In the presence of monomers (in the absence of oxygen) reactions 10 and 29 compete for HO· radicals. In the work of Evans et al. the polymers formed (from polymerization of acrylonitrile, methyl acrylate, methacrylic acid, ethylene, etc.) were not water-soluble, so that termination of the growing polymer chains would be effected by reaction with other growing polymer chains which coagulate in the form of small polymer particles, rather than by reaction with the water-soluble Fe^{++} or H_2O_2. Kinetic evidence has been given (11, 44) for termination by interaction of active polymer chains. The behavior of the growing polymer radicals, which can react only with one another, differs from that of the radicals formed by dehydrogenation of saturated compounds (the "promoters" and "suppressors" of the previous section), which can react with either hydrogen peroxide or with ferrous iron; in effect, hydroxyl radicals which react according to step 29 may be regarded as "consumed." Evidently as the relative concentration of monomer is increased, more hydroxyl radicals should be consumed, so that the molar reaction ratio would approach 1:1.

Experiments were carried out (2) using a number of different monomers and a wide range of concentrations. In typical experiments, the initial concentration of ferrous iron was 0.1 *M*, and the hydrogen peroxide was about one-third as concentrated. The reaction took place in acid solution; the ferrous iron left was titrated with dichromate after 15 minutes. The acidity, method of mixing, and similar experimental details are not given in these papers (2,11). The results obtained are in accord with the above picture; the upper limit of the molar reaction ratio of hydrogen peroxide to ferrous iron with increasing concentrations of monomer was found to be unity.

In the presence of both oxygen and monomers, induced oxidation of the ferrous iron was found (2); the following mechanism was proposed.

$$\mathrm{HO(CH_2CHX)_n\cdot \ + \ O_2 = HO(CH_2CHX)_n\text{-}O\text{-}O\cdot} \qquad (31)$$



$$\mathrm{HO(CH_2CHX)_{n-1}CH_2\overset{\overset{\displaystyle X}{|}}{C}HOO\cdot \ + \ Fe^{++} = HO(CH_2CHX)_{n-1}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}X + OH^- + Fe^{+++}} \qquad (32)$$

Steps 31 and 32 account for the observed inhibition by oxygen of polymerization. However, the sequence of reactions 7, 29, 30, 31, and 32 actually gives the stoichiometric reaction ratio of iron to peroxide (2.0). Induced oxidation of the ferrous iron must be due to a reaction as the following (in place of step 32):

$$\mathrm{HO(CH_2CHX)_nOO\cdot \ + Fe^{++} + H^+ = HO(CH_2CHX)_nOOH + Fe^{+++}} \qquad (33)$$

followed by reaction of the hydroperoxide with more ferrous iron; compare the preceding section.

The initiation of polymerization by the reaction between ferrous iron and hydrogen peroxide is a strong argument in favor of the free radical mechanism for this reaction. Mechanisms can nevertheless be set down for initiation by tetravalent iron:

$$\mathrm{FeO^{++} + CH_2{=}CHX = FeOCH_2{=}CHX^{++}} \qquad (34)$$

$$\mathrm{FeOCH_2{=}\underset{\cdot}{C}HX^{++} + H_2O = FeOH^{++} + HOCH_2{=}\underset{\cdot}{C}HX} \qquad (35)$$

or:

$$\mathrm{FeO^{++} + H^+ = FeOH^{+++}} \qquad (36)$$

$$\mathrm{FeOH^{+++} + CH_2{=}CHX = Fe^{+++} + HOCH_2{=}\underset{\cdot}{C}HX} \qquad (37)$$

It has not as yet been determined whether polymers prepared according to a peroxide-ferrous iron redox recipe contain chemically bound iron.

The extensive fundamental investigations of German workers on redox recipes have been thoroughly reviewed by Kern (25), and will only be mentioned briefly here. Of special interest are the redox polymerizations carried out in bulk and in emulsion systems. Typical reducing agents which were found to be active in the bulk polymerization of acrylonitrile and its derivatives, with benzoyl peroxide as the oxidizing agent, are phenylsulfinic acid, formic acid, phenylhydrazine, thio-β-naphthol, and benzoin.

Two alternative mechanisms are suggested by Kern to account for initiation by systems such as these. In the first scheme, two radicals are formed by direct reaction between the organic peroxide (which may be represented as POOP) and the organic reducing agent (YH_2):

$$\mathrm{POOP} + \mathrm{YH_2} = \mathrm{PO\cdot} + \mathrm{POH} + \mathrm{YH\cdot} \tag{38}$$

Polymerization would be initiated by reaction of the monomer with the radical PO·, and possibly by reaction with YH·. In the second scheme, it is assumed that traces of heavy metals are present, which are oxidized by the peroxide, and reduced by the reducing agent, free radicals being formed in the former reaction (as well as possibly in the latter). This hypothesis, which is of particular importance in emulsion polymerization recipes, is discussed further below.

In studying emulsion polymerization recipes, the German workers found that addition of various organic reducing agents to alkaline recipes containing oxidizing agents such as benzoyl peroxide, hydrogen peroxide, or ammonium persulfate, frequently gave a marked increase in ratio of conversion, and that a further increase was in many cases brought about by the further addition of metallic salts. In most cases these increases in rate of conversion only took place if some complexing agent, such as sodium pyrophosphate, was present in the recipe. As Kern (25) mentions, this points to the mechanism, given above, of catalysis by heavy metal salts as being operative even when such salts are present only as trace impurities.

An emulsion polymerization recipe has recently been reported by Vandenberg and Hulse (47), which is similar to those under study in Germany at the end of the war. In this recipe, butadiene and styrene are the monomers, the emulsifier is a disproportionated rosin soap, some mercaptan is added to control the molecular weight of the polymer, and the redox system consists of cumene hydroperoxide, fructose, and ferric iron, together with sodium pyrophosphate to keep the iron in solution. The use of cumene hydroperoxide and of rosin soap are the chief differences between this recipe and those developed by the German workers, who generally used benzoyl peroxide, and various synthetic detergents, chiefly sulfonates. Recipes employing benzoyl peroxide as oxidizing agent, together with iron pyrophosphate and sugars, have been reported by Marvel and co-workers (38) and by Johnson and Bebb (23). A recipe in which hydrogen peroxide is the oxidizing agent taken in the charge has been described by Marvel and co-workers (37), who reported, however, that in charges prepared according to this recipe, polymerization does not begin until the hydrogen peroxide is completely consumed; accordingly the active oxidizing agent in this recipe is presumed to be an organic peroxide formed in the charge by reaction of soap, or other ingredients, with hydrogen peroxide.

We have studied a recipe similar to that of Vandenberg and Hulse, but with pure saturated fatty acid soap in place of rosin soap, a substitution which not only results in a considerably increased rate of conversion, but removes a possible source of impurities of unknown composition. It appears certain that in these recipes the ferric iron, which is present in the aqueous phase as the pyrophosphate complex, is reduced by the sugar; the ferrous iron thus formed reacts with cumene hydroperoxide, probably with the formation of an organic radical, $C_6H_5\underset{O\cdot}{C}(CH_3)_2$, as discussed in the previous section. It is not certain whether this reaction takes place in the aqueous phase, or in the organic phase, where the iron may be present as the iron soap. If ferrous iron is used rather than ferric iron, we have found that the molar reaction ratio of cumene hydroperoxide to ferrous iron is close to unity, in agreement with the results of Baxendale, Evans, and Park (2).

In these emulsion polymerization recipes, the rate of conversion depends much more strongly upon the concentrations of soap and of sugar than upon the concentrations of other ingredients. Discussion of the role of soap is beyond the scope of this paper; the dependence upon sugar concentration, however, is clearly linked with the rate of reduction of ferric iron. We have studied both the rate of conversion and the rate of consumption of cumene hydroperoxide as functions of the concentrations of soap and of sugar and will report on these effects in a later publication. We may mention that an improved rate of conversion may be obtained in a typical recipe by replacement of fructose with a crude reaction mixture prepared by the Fenton oxidation of glycerol or various sugars. Details will be given in a subsequent publication.

A point of similarity between redox polymerizations and the Fenton oxidation of compounds such as glycerol is that in both cases, the iron is continually being oxidized by the peroxide, and reduced by a sugar or other reducing agent. Active intermediates formed in the course of the peroxide-iron reaction initiate polymerization, in one case, and oxidation, in the other.

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Synopsis

Various mechanisms which have been proposed for the reaction between ferrous iron and hydrogen peroxide are reviewed. Two of these mechanisms appear equally satisfactory on the basis of present evidence: that of Bray and Gorin, involving formation of tetravalent (ferryl) iron, and that of Haber and Weiss, involving formation of hydroxyl and perhydroxyl radicals. Mechanisms involving these intermediates have been developed for the ferric iron-catalyzed decomposition of hydrogen peroxide; the mechanism of Bray and Gorin appears satisfactory, while that of Haber and Weiss leads to certain inconsistencies. A mechanism with ferrous iron and hydroxyl and perhydroxyl radicals as intermediates is presented, which accounts for the experimental observations in the ferric iron-catalyzed decomposition of hydrogen peroxide. The reaction between hydrogen peroxide and ferrous iron induces the reaction between hydrogen peroxide and various organic compounds; this induced reaction (termed a Fenton reaction) is a chain reaction which is initiated by the active intermediates (ferryl iron or hydroxyl radical) formed in the primary reaction. The determination of hydrogen peroxide by reaction with ferrous iron, if carried out in the presence of various organic compounds (termed promoters), gives incorrect results, due to induced oxidation of the promoters; other compounds, termed suppressors, reduce the extent of this induced oxidation of promoters. It appears that both types of compounds react with ferryl iron or hydroxyl radical to form radicals, which if formed from promoters, reduce ferric iron or hydrogen peroxide, while the radicals formed from suppressors oxidize ferrous iron. These considerations are of particular importance in the determination of organic hydroperoxides. The reaction between hydrogen peroxide or organic peroxides and ferrous iron can induce, or initiate, the polymerization of vinyl monomers; this is an example of redox polymerization, which is of considerable practical importance at present.

Résumé

Les différents mécanismes, proposés pour la réaction du fer ferreux-eau oxygénée sont passés en revue. Jusqu' ici deux mécanismes semblent également satisfaisants: celui de Bray et Gorin, qui suppose la formation de fer tétravalent (ferryl), et celui de Haber et Weiss, qui suppose la formation de radicaux hydroxyles ou perhydroxyles. Des mécanismes, comportant ces intermédiaires, ont été développés pour la décomposition de l'eau oxygénée, catalysée par le fer ferrique. Le mécanisme de Bray-Gorin semble satisfaisant, tandis que celui de Haber-Weiss présente certaines difficultés. Dans ce travail, un mécanisme, comportant du fer-ferreux et des radicaux hydroxyles et perhydroxyles, comme intermédiaires, est développé; il répond aux observations expérimentales, dans la décomposition catalytique du peroxyde d'hydrogène par le fer ferrique. La réaction entre le peroxyde d'hydrogène et le fer ferreux induit les réactions entre l'eau oxygénée et de nombreux composés organiques; cette réaction induite, appelée réaction Fenton, est une réaction en chaîne, qui est initiée par les intermédiaires actifs (fer ferrylique ou radical hydroxyle) formés dans la réaction primaire. La détermination du peroxyde d'hydrogène par réaction avec le fer ferreux donne des resultats incorrects, si elle est effectuée en présence de différentes substances organiques, denommées promoteurs; cet effet est dû à une oxydation induite des promoteurs eux-mêmes. D'autres composés, appelés des "suppres-

sors" (inhibiteurs) diminuent par contre cette oxydation induite des promoteurs. Il semble que les deux types de dérivés réagissent avec le fer ferrylique ou les radicaux hydroxyles pour former des radicaux, lesquels, s'ils proviennent des promoteurs, réduisent le fer ferrique ou l'eau oxygénée, tandis que les radicaux formés au depart des "suppressors" oxydent le fer ferreux. Ces considérations sont importantes pour la détermination des hydroperoxydes organiques. La réaction entre le peroxyde d'hydrogène ou des peroxydes organiques avec le fer ferreux peut induire, ou initier, la polymérisation des monomères vinyliques; ceci constitue un exemple de la polymérisation redox, qui est à l'heure actuelle d'une importance pratique très considérable.

Zusammenfassung

Verschiedene Mechanismen, die fuer die Reaktion von zweiwertigen Eisen und Wasserstoffsuperoxyd vorgeschlagen wurden, werden eroertert. Zwei dieser Mechanismen scheinen zu sein auf Grund gegenwaertiger gleichmaessig befriegend Evidenz; der von Bray und Gorin, in dem die Bildung vierwertigen Eisens (Ferryl) angenommen wird, und der von Haber und Weiss, in dem die Bildung des Hydroxyl- und Perhydroxylradikals vermutet wird. Mechanismen mit diesen Zwischenprodukten wurden fuer die durch Ferri-Eisen katalysierte Zersetzung des Wasserstoffsuperoxydes entwickelt; der von Bray und Gorin vorgeschlagene Mechanismus ist zufriedenstellend wogegen der von Haber und Weiss zu gewissen Widerspruechen fuehrt. Ein Mechanismus mit Ferro-Eisen, Hydroxyl- und Perhydroxyl-Radikalen als Zwischenprodukten wird vorgeschlagen, der mit experimentellen Beobachtungen der durch Ferri-Eisen katalysierten Zersetzung von Wasserstoffsuperoxyd uebereinstimmt. Die Reaktion zwischen Wasserstoffsuperoxyd und Ferro-Eisen induziert die Reaktion zwischen Wasserstoffsuperoxyd und verschiedenen organischen Verbindungen; diese induz. Reaktion (die Fenton-Reaktion genannt wird,) ist eine Kettenreaktion, die durch aktive Zwischenprodukte (Ferryl-Eisen oder Hydroxylradikale) die in der primaeren Reaktionsstufe gebildet werden, hervorgerufen wird. Die Bestimmung von Wasserstoffsuperoxyd durch die Reaktion mit Ferro-Eisen, falls sie in Begenwart verschiedener organischer Verbindungen stattfindet, ergibt falsche Resultate wegen derer induzierten Oxydierung. Es scheint, dass beide Klassen von Verbindungen mit Ferryl-Eisen oder Hydroxylradikalen reagieren und so Radikale bilden, die im Falle der ersten Klasse von Verbindungen Ferryl-Eisen oder Wasserstoffsuperoxyd reduzieren, wogegen Radikale, die von der zweiten Klasse entstanden sind, Ferro-Eisen oxydieren. Diese Betrachtungen sind von besonderer Wichtigkeit in der Bestimmung organischer Hydroperoxyde, Die Reaktion zwischen Wasserstoffsuperoxyd oder organischen Peroxyden mit Ferro-Eisen kann die Polymerisation von Vinylmonomeren induzieren oder hervorrufen; dies ist ein Beispiel der zur Zeit wichtigen Redox-Polymerisation.

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Journal of Polymer Science Vol. IV, pp. 399-400, 1949

LETTER TO THE EDITORS

NOTE ON THE "INHOMOGENEITY" OF POLYMERS

Schulz (1) defined the inhomogeneity of a polymer sample by the following expression:

$$U = \frac{P_w}{P_n} - 1$$

Though this equation serves as a guide in many cases, e.g., degradation of polymers, it may be quite misleading in others.

This may be illustrated by a specific example. Consider the case of polymerization consisting of an uncatalyzed bimolecular initiation reaction, termination brought about by disproportionation. The inhomogeneity for this case is $U = 1$. (Compare Bawn (2) p. 78.) According to the above definition this inhomogeneity should be the same irrespective of the individual magnitudes of P_w and P_n; that this is not the case can easily be demonstrated. Consider a polymer sample of $P_w = 500$, $P_n = 250$, and one having the values $P_w = 2000$, $P_n = 1000$. The general weight distribution function is given by:

$$m_P = P\varepsilon^2\left(\frac{1}{1 + \varepsilon}\right)^P$$

Where m_P is the weight fraction, P the chain length, and ε a constant containing the rate constants of the polymerization. In the first case, $\varepsilon = 4 \times 10^{-3}$, in the second, $\varepsilon = 1 \times 10^{-3}$. Fig. 1 (p. 400) gives the two relevant weight distributions. It is apparent from these curves that the inhomogeneities of the two curves are not identical; however, according to equation 1 they would be classed as being of the same inhomogeneity.

It would be more appropriate to measure the inhomogeneity of polymers by their "spread" as follows (3):

$$U = \sigma^2 = \text{number average (weight average - number average)}$$
$$= P_n(P_w - P_n)$$

where σ is the root mean square deviation for the number distribution. For the case mentioned above the relevant values are:

$$\sigma_1^2 = 6.25 \times 10^4 \text{ for } P_w = 500,\ P_n = 250$$

$$\sigma_1^2 = 1 \times 10^6 \text{ for } P_w = 2000,\ P_n = 1000$$

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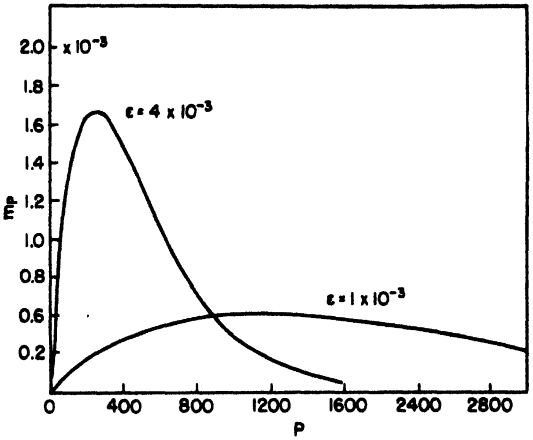

Fig. 1. Weight distribution curves according to distribution function $m_P = P\varepsilon^2(\frac{1}{1+\varepsilon})^P$.

Journal of Polymer Science Vol. IV, pp. 401-403, 1949

LETTER TO THE EDITORS

MOLECULAR WEIGHT METHODS

Under certain conditions, simplified procedures appear possible in the characterization of polymers by number-average and weight-average molecular weights. These methods are made obvious by elimination of the osmotic slope, B, between the simplest osmotic pressure and light-scattering equations for dissolved polymers (1),

$$\frac{\pi}{c} = \frac{RT}{\overline{M}_n} + Bc \tag{1}$$

$$\frac{Hc}{\tau} = \frac{1}{\overline{M}_w} + \frac{2Bc}{RT} \tag{2}$$

(π = osmotic pressure, c = concentration, R = gas constant, T = absolute temperature, B = slope, $\overline{M}_n$ = number-average molecular weight, H involves optical constants of the system, τ = turbidity, and $\overline{M}_w$ = weight-average molecular weight.)

Equations resulting from such manipulation are, for polydisperse systems,

$$\frac{1}{\overline{M}_n} = \frac{\pi}{RTc} - \frac{Hc}{2\tau} + \frac{1}{2\overline{M}_w} \tag{3}$$

or, defining $\overline{M}_w$ by

$$\frac{1}{2\overline{M}_x} = \frac{1}{\overline{M}_n} - \frac{1}{2\overline{M}_w}, \tag{4}$$

$$\frac{1}{2\overline{M}_x} = \frac{\pi}{RTc} - \frac{Hc}{2\tau}, \tag{5}$$

and monodisperse systems, where $M = \overline{M}_n = \overline{M}_w$,

$$\frac{1}{M} = \frac{2\pi}{RTc} - \frac{Hc}{\tau} \tag{6}$$

These relations approach complete validity only when equations 1 and 2 adequately represent the behavior of the particular polymer-solvent system at values of c up to and including the highest under consideration. Although considerable theoretical advance has been made in estimating the importance, relative to Bc, of the terms involving higher powers of c in the generalized equation for the reduced osmotic pressure of a polymer-solvent system (2), the adequacy of equations 1 and 2 should at present be established experimentally. For the purpose of molecular weight measurement procedures proposed here, the most concentrated solutions satisfying equations 1 and 2 should be used, and best sensitivity would be obtained in a poor solvent, or a solvent-nonsolvent mixture, so that the value of B is small, and π and τ are more dependent on molecular weight and the first power of the concentration. The application of these relations to molecules sufficiently extended to show interference in the scattered light is not considered here.

When the conditions of the preceding paragraph can be met, it appears that equation 3 would enable the calculation of the true extrapolated value of either $\overline{M}_n$ or $\overline{M}_w$ from the extrapolated value of the other plus one measurement of turbidity or osmotic pressure. This would have the effect of extending the region of accuracy for both $\overline{M}_n$ and $\overline{M}_w$ determinations. For example, the value of $\overline{M}_w$ for a high molecular weight polymer is easily measured by light scattering involving extrapolation by means of equation 2. However, the usual determination of $\overline{M}_n$ would involve extrapolation of inaccurate π/c values in dilute solution. By use of equation 3, the solution of highest concentration used for measurement of τ could be subjected to a single measurement of π, then these values plus that of $\overline{M}_w$ could be used for the calculation of $\overline{M}_n$. Conversely, low molecular weight polymers are easily measured for $\overline{M}_n$, but are too low in $\overline{M}_w$ to yield accurate values from the usual light-scattering measurements. In this case the extrapolated value of $\overline{M}_n$ would be used in equation 3 with single values of τ and π taken in the solution of highest concentration used. It is expected that procedures of this kind would find most use where routine measurements on the same kind of polymer are carried out. In this case the preliminary determinations of the best solvent system to be used, of the adequacy of equations 1 and 2, and of the reliability of π and τ measurements at various concentrations would appear to be justified. In some polymer-solvent systems, undesirable association among polymer molecules and slow osmosis may be encountered.

The use of another kind of average molecular weight, $\overline{M}_x$, as defined for equation 5, is suggested for application to polydisperse systems. Within the limitations imposed, the calculated value of $\overline{M}_x$ would be independent of the concentration used for its determination and would require only one value each for turbidity and osmotic pressure from the same solution. It should, therefore, be a useful and conveniently determined characteristic of the polymer without separate determination of $\overline{M}_n$ or $\overline{M}_w$. The value of $\overline{M}_x$ should always lie between $\overline{M}_n$ and $0.57\overline{M}_n$ as shown below since $\overline{M}_w \geq \overline{M}_n$:

Size distribution	$\bar{M}_w/\bar{M}_n$	$\bar{M}_x$
Monodisperse	1	M_n
Medium polydispersity	2	$2/3\ \bar{M}_n$
Wide polydispersity	∞	$1/2\ \bar{M}_n$

In the possible instance of a monodisperse system of polymer molecules, equation 6 indicates that the true extrapolated value of the molecular weight can be determined from values of π and τ at a single concentration without extrapolation. Thus, the highest concentration that satisfies the limiting assumptions can be used for highest accuracy. Application of equation 6 should be of interest in fractionation studies.

Appreciation is expressed to Dr. J. B. Nichols and Prof. F. T. Wall for helpful discussions of this subject.

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REVIEW

"The Chemistry of the Polysaccharides." Robert J. McIlroy. Longmans, Green, London, 1948, 118 pp., $2.50.

This little book of approximately one hundred pages is a rather heterogeneous collection of brief essays on the polysaccharides and related topics. Emphasis is placed upon structural concepts, and the presently incomplete status of the structure of the natural polysaccharides is delineated. The general methods that have been employed are well described, and the chemistry of the monosaccharides is elaborated to the extent required to recognize them as polysaccharide component units. The large and increasing size of the group of natural polysaccharides is well shown. Some analytical methods are given in experimental detail and an appendix is added to report a few selected recent advances. The book is recommended for those wishing to make a quick and cursory review of this significant research field.

M. L. Wolfrom

Journal of Polymer Science Vol. IV, pp. 405-407, 1949

LETTER TO THE EDITORS

DEGRADATION OF HIGH POLYMERS *

Since the resistance of a high polymeric substance to degradative processes is often a most important consideration governing both the molecular weight attainable in a polymerization reaction and the stability of the product, the relation between rate of degradation and molecular weight (or degree of polymerization) is a matter of some interest. In the following derivation such a relation is developed.

A linear polymeric molecule may be described as consisting of monomeric units held together by polymer linkages, the number of which we shall designate by p. For a single molecule, $p = n - 1$, where n is the degree of polymerization (number of monomer units per molecule). In a system consisting of polymer of (infinitely) high molecular weight, the number of polymer links in a given volume may be designated by p_∞. As such a polymer is subjected to degradation, each link destroyed is replaced by two end groups; and thus at any time,

$$p_\infty = p + \frac{1}{2}\epsilon \tag{1}$$

where ϵ gives the number of end groups.

Since the number of polymer chains present is $\epsilon/2$ and the average number of polymer links per chain is $2p/\epsilon$, the average degree of polymerization is given by:

$$n = \frac{2p}{\epsilon} + 1 \tag{2}$$

Combining this with equation 1 we obtain:

$$p = p_\infty\left(\frac{n - 1}{n}\right) \tag{3}$$

If degradation is a first-order reaction (as would be the case, for example, were chain rupture due solely to intramolecular thermal stresses), the rate of destruction of polymer links at some given temperature is:

$$-\frac{dp}{dt} = kp \tag{4}$$

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*Contribution from E. I. du Pont de Nemours and Company, Rayon Technical Division, Buffalo, New York.

Integration of equation 4 gives:

$$-\int_{p_\infty}^{p}\frac{dp}{p} = k\int_{0}^{t} dt \quad \text{or} \quad \ln(p_\infty/p) = kt \tag{5}$$

With the aid of equation 3 this may be expressed in terms of the degree of polymerization:

$$\ln\frac{n}{n-1} = kt \quad \text{or} \quad n = \frac{e^{kt}}{e^{kt}-1} \tag{6}$$

Equation 6 gives the degree of polymerization at any time for a polymer initially of very high molecular weight.

Substitution of equation 3 in equation 4 gives:

$$-\frac{dn}{dt} = k(n^2 - n) \tag{7}$$

for the rate of decrease in D.P. As a good approximation at high molecular weight,

$$-\frac{dn}{dt} = kn^2 \tag{8}$$

will hold since n^2 will then be much larger than n. Thus, during a degradation reaction of the first order with respect to reacting groups, the rate of loss of molecular weight (number average) is nearly proportional to the square of the molecular weight.

As a matter of fact, if can be shown that the approximate expression, equation 8, results without the assumption of a first-order degradation reaction. For a more general case, equation 4 may be rewritten:

$$-\frac{dp}{dt} = kp^x \tag{9}$$

where x is the reaction order. By equation 3 this may be expressed in terms of the D. P.:

$$-\frac{dn}{dt} = k'n^2\left(\frac{n-1}{n}\right)^x \tag{10}$$

At high degrees of polymerization $(1 - 1/n)^x$ approaches unity, and equation 10 becomes equivalent to equation 8.

In the above derivation it has been assumed that the chemical bond destroyed is that joining monomer units; however, if the bond actually broken is a different one, the expressions in terms of D. P. will still be valid. The approximate relation, that the degradation rate of a polymer is proportional to the square of its number-average molecular weight, should hold for any thermal degradation unless the total reaction rate is a composite of the rates of several different reactions. In this case, the relation should still be applicable over any part of the degradation curve where one reaction is proceeding much more rapidly than the others or where the different reactions are proceeding at essentially the same rate. It should also prove valid for chemical degradation in a constant environment; e.g., hydrolysis in dilute polymer solutions. It has been a tacit assumption in the foregoing derivation that degradation is carried out under conditions where no polymerization can occur and that the strength of the bonds in question is independent of the size of the molecules in which they occur.

In order to test the accuracy of these derived equations, it would be necessary to have data on number-average molecular weight at various stages of degradation of the polymer. Such data are not available, but the data given in Table I show the variations of intrinsic viscosity of polyethylene terephthalate after various times of heating at 285°C. The exact relationship between intrinsic viscosity of this polymer and number-average molecular weight is not known, but it seems reasonable to assume that these data show a qualitative agreement with the requirements of the derived equations.

TABLE I. Thermal Degradation of Polyethylene Terephthalate at 285°C.

Heating time, hours	Intrinsic viscosity 1	Intrinsic viscosity 2
0	0.58	0.75
1	0.44	0.55
2	0.41	0.45
3	0.39	0.42
4	0.37	0.40

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ERRATA

Errata: PHOTOCHEMISTRY OF PROTEINS. V. EFFECT OF pH AND UREA ON ULTRAVIOLET LIGHT INACTIVATION OF CRYSTALLINE PEPSIN

(J. Polymer Sci., 4, 45-62, (1949)

by A. D. McLaren and Sidney Pearson
Institute of Polymer Research, Polytechnic Institute of Brooklyn, Brooklyn, New York

Page 45, lines 15-16 should read:

> (11) If the former is true, the increased accessibility of tyrosine residues in the presence of urea might also result in a reduction of any screening effect of chromophoric groups about the vital tyrosine

Page 46, line 31 should read:

> digested at 24.1°C. After 10 minutes the enzyme and undigested pro-

Page 48, line 10 under Table II, should read:

> deflection represented 8.84 x 10^{-6} watts/cm.^{2}. With the reaction cell

Page 50, lines 4 and 8 under equation (1):

> change 2700 to 2770

Errata: ADHESION. III. ADHESION OF POLYMERS TO CELLULOSE AND ALUMINA

(J. Polymer Sci., 4, 63-74, 1949)

by A. D. McLaren and Charles J. Seiler
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Title should read:

> ADHESION. III. ADHESION OF POLYMERS TO CELLULOSE AND ALUMINUM

Page 66, Table III, column 2, should read:

Mole fraction MVK
0.0
0.27
0.51
0.69
0.86
1.00

Page 67, equation (2) should read:

$$\ln \eta_1 = \ln \eta_2 = A_1 + CM_1^{1/2} + B/T_1 = A_2 + CM_2^{1/2} + B/T_2$$

Journal of Polymer Science Vol. IV, pp. 409-410, 1949

REVIEW

"Principles of High Polymer Theory and Practice." Alois X. Schmidt and Charles A. Marlies. McGraw-Hill, New York, 1948, xii+743 pp., $7.50.

The science of large molecules encompasses not only the naturally occurring materials–wood, cotton, wool, silk, polysaccharides, protein, rubber, and many others–but also the ever-increasing range of synthetic organic polymers. The intense interest in this field has led to a rapid growth in publication, and there have appeared, on the one hand, a number of technological and industrial monographs which pay little attention to the fundamentals and, on the other, a series of monographs often of a specialized nature and dealing with the fundamental aspects.

In the present work the authors have attempted to fuse both aspects and have produced a textbook which explains not only the elementary principles and concepts but also the manufacture, development, fabrication, and application of high polymeric materials. The contents are arranged to suit both the undergraduate and graduate courses and it is suggested that certain chapters may be by-passed and others be regarded as optional depending on the length of the course. No part of the book, however, is beyond the range of the student with the normal degree of training in chemistry.

Introductory chapters on definitions and concepts and the nature of molecular forces are followed by four chapters on the special properties, formation, and structure of high polymers. The next section of the book comprises chapters on rheology, molding and manipulations, mechanical properties, and the electrical, thermal, and optical properties. The final part deals with the special properties and applications and includes chapters on fibers, rubber, surface coatings, adhesives, and resins. The whole field of polymeric materials is covered. No topic of importance seems to be omitted.

In spite of this enormous task and the wealth of useful and accurate information in this book, the reviewer has difficulty in deciding for what class or type of student this textbook is intended. He is of the opinion that before embarking upon the special study of high polymers a thorough grounding in physics and chemistry is essential. From this point of view much of the elementary chemistry in the book could be omitted or considerably condensed and the treatment of the more fundamental ideas of the polymerization process, and the thermodynamics and the methods of studying molecular shape and size, extended and developed. Much of the latter part of the book on the applications, although summarizing much factual and technical knowledge that may be useful to the technologist or chemical engineer, is divorced in its outlook from the elementary presentation of fundamental principles of polymeric materials developed in the early half of the book. For example, while it is accepted that the fabrication processes are governed by rheological behavior, the chapter on mixing, extrusion, spinning, etc. Like many other sections in the book this serves to illustrate the very wide gulf between pure research and technological problems in the polymer industry.

The book as a whole is clearly written and well illustrated, and at the end of each chapter an adequate selection of references to review articles and monographs is given. The extensive references to trade information in both the text and the appendices seem to be unnecessary in a textbook of this type.

In summary, the book attempts too much in trying to cover the chemistry, physics, mechanics, manufacture, and application of high polymeric materials. It should, however, prove useful to the technologist who wishes to obtain some knowledge of the basic principles and to the chemist unfamiliar with the application and use of natural and synthetic polymers.

C. E. H. Bawn

REVIEW

"Advances in Protein Chemistry, Volume IV." M. L. Anson and John T. Edsall, editors. Academic Press, New York, 1948. 575 pp., $8.50.

The latest volume in this series of reviews on protein chemistry contains eight contributions, describing substances ranging from simple amino acids to complex gel networks.

Of particular interest to the polymer chemist is the discussion on protein gels by J. D. Ferry. Greatest attention is paid to the properties of gelatin and fibrin, fields to which the author has contributed substantially himself. A description is given also of gels formed by egg albumin, insulin, casein, and other proteins. Throughout this review, the theory of network formation is used to correlate the observed mechanical and optical behavior of these systems.

Equally of interest to the polymer scientist concerned with proteins are the articles by Corey, Svensson, Putnam, and Wyman. In a brief but lucid article, R. B. Corey summarizes the information which has been obtained from x-ray studies on amino acids and peptides, and the inferences which may be made from these investigations on the molecular configurations within proteins. Unfortunately, however, this article seems to have been written before the publication (1947) of the striking work of Perutz and his associates on crystalline hemoglobin, since no mention is made by Corey of these brilliant investigations.

In an article replete with diagrams, H. Svensson surveys ionophoresis and electrophoresis as preparative methods. Fractionation procedures are described for isolating amino acids. Much attention is devoted also to the Tiselius electrophoresis apparatus as an instrument for protein fractionation, and a detailed description is given of the most recent type of cell used for preparative purposes.

A very comprehensive survey of complexes of proteins with detergents has been prepared by F. W. Putnam. Information from various methods of investigation has been brought together and used to establish a reasonable interpretation of the mechanism of the observed interactions.

The most impressive contribution in the present volume is the critical review by J. Wyman on the heme proteins. In addition to the discussion of the descriptive aspects of the properties and behavior of these proteins, there is presented a method of correlation of the quantitative aspects of the behavior of hemoglobin in terms of generalized functions for the treatment of complex equilibria, which clearly is the definitive work in this field. Much of the theoretical discussion could be carried over profitably to other colloidal phenomena.

In addition to the five reviews mentioned so far, there are three articles of lesser interest to the polymer chemist on proteins of pathogenic origin, the distribution of plasma proteins in disease, and the stereochemistry of amino acids.

As in previous volumes, each article in the present edition contains an extensive outline which most readers will find of definite value in placing each topic into the general picture. The large number of diagrams, particularly in the reviews by Corey and Svensson, also add substantially to the clarity of presentation. The particular topics chosen by the editors represent a reasonable selection from the broad field of protein chemistry. Investigators interested in the special fields included among these topics will find the articles comprehensive and critical; colloid and polymer chemists in general will find these reviews very stimulating and suggestive.

I. M. Klotz

REVIEW

"Theory of the Stability of Lyophobic Colloids. The Interaction of Particles Having an Electric Double Layer." E. J. W. Verwey and J. T. G. Overbeek, with the collaboration of K. van Ness. Elsevier, New York-Amsterdam, 1948, 216 pp., $4.50.

This important work describes a mathematical and physical theory developed by the authors during the German occupation of Holland, and is presented here for the first time in complete form. It consists of three parts, as follows: Part I, Theory of a Single Double Layer; Part II, On the Interaction of Two Parallel Flat Plates; Part III, On the Interaction of Spherical Colloidal Particles. There is also an appendix entitled "Theoretical Work on the Stability of Lyophobic Colloids by Previous Authors."

It is not to be expected that such a detailed theoretical treatment should provide easy reading. The authors have, however, alleviated the burden of strict logic by a parallel discussion which explains how their derivations differ from those of previous workers. This valuable feature runs throughout the text and provides also the main topic in the appendix. The English is commendably good; here and there one finds slight departures from our customary usage which add a touch of piquancy without seriously endangering the meaning. The authors have made extensive use of graphical methods in presenting their results.

The chief practical advantages claimed for this theory are that it predicts the Schultz-Hardy valency rule in coagulation, and also explains how, at the proper concentrations, colloidal systems can show thixotropy and tactoid formation. The contributions of ionic and nonionic factors to the resultant forces between particles are made clear throughout. Especial emphasis is placed on the nonionic factors, that is, on the molecular attractions that go by the name of London-van der Waals' forces. It is believed that their range in colloidal systems is much greater than that found for colliding molecules in the kinetic theory of gases. For parallel plates, for instance, the force falls off inversely as the square of the distance, whereas for pairs of gas molecules it diminishes inversely as the seventh power of the distance. Thé evaluation of this force is the least precise part of the authors' treatment and in combining it with the electric forces due to ions certain values are empirically adopted.

Those concerned with polymer chemistry have, in general, tended to neglect the London-van der Waals' forces and to place their chief emphasis upon chemical linkage. In systems where the process of condensation has come to an end without producing an indefinitely extending structure it would seem that these forces could be extremely important. In addition, all that group of colloidal electrolytes, which is sometimes called "polyelectrolytes," comes within the general scope of this book. However, the forces between linear particles in suspension are not evaluated, whereas plates and spheres are fully covered; there would seem to be room here for extremely useful extensions of the authors' treatment.

In general, therefore, this work will, through its detailed examination of the nature of the forces between colloidal particles, exert an important influence upon future developments. It is not to be doubted that some of these will be concerned with the colloid chemistry of polymers. The publishers are to be congratulated in making this fundamental work generally accessible.

C. E. Marshall

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REVIEW

"Plastics Dictionary." Thomas A. Dickinson. Pitman, New York, 1948, xiii +312 pp., $5.00.

According to the author, the purpose of this dictionary is to provide both the expert and the layman with understandable definitions of terms generally used with reference to plastics. It contains approximately 3,500 definitions and several tables and charts recording data on catalysts, chemical elements, fillers, pigments, plasticizers, and solvents, and lists many of the books and periodicals in this field. Include are numerous definitions of foreign trade names, with emphasis on those originating in Great Britain.

Although it does fulfill partially the need for a reference book of this type, many of the definitions appear to be incorrect, confusing, or inadequate. Therefore, it can hardly be recommended for the layman, who might not be able to recognize its defects. The expert will find a fresh viewpoint in some definitions with which he is familiar, but should not have confidence in unfamiliar definitions. Frequently, when a resin or apparatus is defined, the author lists only one manufacturer and does not infer that there are others who are perhaps equally or even more widely known. A few examples of unsatisfactory definitions are the following:

Acrylonitrile: "It may serve as either a monomer or polymer." - ?

Adipic: " - soluble in water, alcohol and ethyl." - Ethyl what ?

Amides: "Same as amines." - ?

Ion: "Positively charged ions are called anions, and negatively charged ions are called cations." - ?

Detergent: "A compound that purifies or cleanses."

Dielectric: "A material that resists the flow of an electrical current."

Dryer: "A machine or device designed to be used in separating liquids from solids....(see drying agent.)" - ?

Drying Agent: "A metallic soap of one of the higher organic acids used to hasten the hardening or curing of resins. Japan dryer is the agent most frequently used to speed the hardening of coatings. (See dryer.)" - ?

Fade-o-meter: "An electrical device produced by Willmott, Son, & Philips, Ltd., Great Britian." - How about manufacturers in U. S. A. ?

Tung Oil: "A yellow oil obtained from the fruit of aleurites cordata." - Many experts would not recognize this definition.

Silicones: "A comparatively new group of plastics developed by Dow Corning Corp., U.S.A." - How about General Electric?
Lacquer: "Natural and/or synthetic resin suspended in readily evaporating solvents." - ?
Latex: "A vegetable resin or juice, or an unvulcanized elastomer." - ?
Moisture Permeability: "See moisture absorption."
Zerex: "A polyvinyl alcohol antifreeze compound-----" - ? This should be ethylene glycol!

G. W. Seagren

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Some Remarks on the First Interaction Coefficient of the Viscosity-Concentration Equation

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INTRODUCTION

The problem of the relation between relative viscosity and concentration of colloidal or polymer solutions is one of old standing. It is intimately linked up with the viscosity of liquids and of liquid mixtures. With all details of molecular structure and force fields coming into play, no simple general solution can be expected. A considerable simplification is possible though whenever the particles of one component are large enough and have a shape sufficiently well defined to consider them as submerged bodies. The system can then be treated hydrodynamically. In doing this for a suspension of spheres, Einstein (1) derived the equation that proved so eminently fruitful but applies to dilute systems only. Since then, using the same approach, Jeffery (2), Kuhn (3), Guth (4), Simha (5), Huggins (6), Kirkwood and Riseman (7), Debye (8), and others successfully developed equivalent equations for ellipsoids, rods, dumbbells, kinked chains and coils for the case of overiding Brownian movement, but again only in dilute solutions where the contributions of individual particles are additive.

On the other hand, there are the great number of attempts to formulate concentration effects empirically, or to deduce a relation from special assumptions (9). Frequently, authors have started from one of the theoretical linear relations, trying to modify them for interaction, overlooking that thereby they violated the basic assumption from which the linear laws were derived. However, it was soon recognized that, as in other cases, a series of powers in the concentration was most suitable to describe concentration effects. Those of a polynomial structure, or representing an expanded logarithm, as, for example, Hess and Philippoff's (10) or Martin's (11) equation, were especially successful in describing the viscosity over a wide range, though at moderate concentration only the square, or at best the cubic term, need to be considered. At the other end of the concentration scale Flory's (12) equation for pure molten polymers should be mentioned, as well as Eyring's (13) attempt to use it for a formulation of composite viscosities.

The first to take up Einstein's approach for the calculation of the effect of concentration was Guth, who with Gold (14) and Simha (15) calculated the coefficient of the square term, finding a value 14.1. Unfortunately, external circumstances together with the mathematical difficulties did not permit the calculation of higher coefficients for spheres, nor of any for the concentration effects of nonspherical particles. At least it became clear that the powers of the concentration should be the consecutive integers, that is, c^2, c^3, or perhaps c^4 for spheres, and also a c^2 and c^3 for ellipsoids. Simultaneously the experimental re-investigation of the viscosities of suspensions, carried out by one of the authors (16) by means of models, largely confirmed the theoretical work. In addition, the coefficient of the cubic term for spheres was found to be approximately $2.(2.5)^3$. Further, it turned out that for large rigid rods, too, the coefficients for the higher concentration terms could be represented by that of the linear term to the same power as c, times a numerical factor near unity. This agreed with Guth's expectation and indicated the interesting possibility that the viscosity contribution due to interaction of particles of any shape could to a certain extent be represented by hydrodynamically effective spheres (similar to resistance problems), the radius of which, for incipient concentration effects, might remain reasonably constant.

Subsequently it has become common practice to designate with Kraemer the factor of the linear term, as found by extrapolation from the experiments, as the intrinsic viscosity. Huggins (17) has finally brought the viscosity-concentration relation into its present form, which incorporates all the features discussed above and has a wide applicability for high polymer solutions of moderate concentration. Huggins noticed that the coefficient of $[\eta]^2c^2$, k' in his notation, though constant with molecular weight, changed significantly for the same polymer fraction in different solvents, in a way opposite to the intrinsic viscosity. He observed also that k' changed in the same way as the constant μ in his thermodynamic theory of polymer solution. This behavior is of considerable interest and has stimulated various efforts for its interpretation, none so far conclusive. Since a better insight should be of great value for our understanding of concentrated polymer solutions, it seems desirable to re-open the discussion in the light of a few recent observations.

SIGNIFICANCE OF k'

The coefficient k' was introduced by Huggins, and before, independently, by Kuhn (3), as a hydrodynamic correction factor. In the use of Stokes' law to calculate the viscosity contribution from the resistance of the molecular chains, an appreciable error enters on account of the deviation of the individual chain members from spherical shape, further on account of their being comparable in size with the solvent molecules, and also from their mutual interaction. The factor k' with which $[\mu]$ is multiplied is assumed to take care of these discrepancies. Huggins introduced further into the Stokes' resistance the viscosity of the solution instead of the solvent in order to cover initial concentration effects. He writes for the viscosity:

$$\eta = \eta_{solution} \doteq \eta_{solvent}\left[1 + k'[\eta]c\right]$$

A similar procedure has been used with advantage by several authors but as discussed later it remains questionable how far this is justified. From here Huggins arrives at this relation:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c + \ldots \cdot$$

where k' appears as the numerical coefficient of the square term.

According to this, k' is of the nature of an independent constant, referring to the units or to a sequence of units in a polymer chain, and possibly to the peculiarities of the chain as regards back-coiling. Therefore, k', while contributing to the intrinsic viscosity, should form a rather constant contribution unaffected by the other factors making up the intrinsic viscosity. This is true for changes of $[\eta]$ with the molecular weight, and, in so far, may be taken as a confirmation of Huggin's assumptions. On changing the solvent, though k' becomes a function of the solvent nature. It appears to us that current attempts to explain this variation are out of line with the definition of k', as originally introduced.

These explanations go back to the general observation that in the best solvents the intrinsic viscosity is usually highest, and decreases with increasing μ-values. Huggins (18) and Alfrey, Bartovics, and Mark (19) were the first to point out that this is probably due to the fact that in good solvents chainlike molecules will be more extended than in bad ones, where residual molecular forces tend to reduce the dimensions of the molecular coil, and thereby its over-all hydrodynamic effectiveness. Conforming with this, the slopes of the η_{sp}/c versus c curves increase with the better solvents and decrease in the lesser ones, but not nearly enough to keep k' constant. To explain this, it has been widely assumed that the smaller effective hydrodynamic radius in the poorer solvents is more than compensated for by the greater number and duration of polymer-polymer contacts in such a solvent, resulting in an increased interaction. This is unlikely in view of the interparticle distances at which concentration effects set in, but even if this explanation were correct, it would still be inconsistent with the original definition as a hydrodynamic effectiveness- and interaction factor, to express these influences as changes in k'[1].

Moreover, the parameter k', as introduced, should in reality appear specifically in the expression for intrinsic viscosity (1), since it is introduced as a factor pertaining to the behavior of a single chain and not of a set of chains. Its consequent appearance, and the manner of its appearance, in the terms relating to the particle interaction,

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[1] Inasmuch as in deriving an expression for the intrinsic viscosity, k' was introduced to correct for the deviations of the frictional resistance of the chain elements from that given by Stokes' law, it should be possible to obtain k' from data defining intrinsic viscosities. Thus on the basis of the Huggins formulation it would appear that the viscosity behavior of concentrated solutions should be predictable from the viscosity behavior of the infinitely dilute solution. In this connection we call attention to the frictional constant ζ introduced in the Kirkwood-Riseman viscosity theory. Comparing k' and ζ we see that the two should be related as follows:

$$k' = \zeta/6\pi\eta_0 a$$

Where η_0 is the solvent viscosity and a the radius of the chain segment. In particular the ratio of k' in two different solvents, should be related to that of ζ in the two solvents. Therefore, knowing the value of k' in one solvent and the intrinsic viscosity in both solvents, we ought to be able to compute k' in the second solvent and consequently, according to Huggins, the concentration dependence of the

(Footnote continued at bottom of page 420)

could be justified only by specifically introducing such interactions into the theory itself. The artifice of bringing in such interaction through the use of a solution viscosity rather than the solvent viscosity in Stokes' law is questionable. Such an artifice does not allow for the fact that the presence of a finite concentration of particles affects the hydrodynamic behavior of the fluid, since obviously the nature of the flow will change. It is this overlapping or additional distortion of the fluid flow due to the large number of particles present that brings about the changes in viscosity which represent a concentration effect basically different from the effect of the addition of further particles to a pure liquid of the same viscosity as the suspension. It is not surprising that such an effect is satisfactorily given by an equation containing an $[\eta]^2$ concentration term as proposed by Huggins, since a dimensional analysis alone would show that such a term should appear. Similarly, a k' term, having among others a significance as that of Huggins, can indeed be expected. However, being the coefficient of a square term k' would be of a necessarily more complex nature, having to do with the actual mechanism of hydrodynamic interaction between particles. It follows that in the absence of a satisfactory theory or of clear-cut experimental evidence, k' will either have to be redefined, or one or several additional interaction constant introduced, or that one would have to revise the exponent of $[\eta]$.

In attempting such a clarification it will be of advantage to remember that primarily we have to deal with slopes, that is, with the coefficient of c^2, which in the plot of η_{sp}/c vs. c becomes the slope of the curve. In order not to be arbitrary in splitting this coefficient into factors, one must have good evidence on theoretical or experimental grounds. As regards the former we have the reasons given above for a near proportionality of the slopes with $[\eta]^2$, and the same relation emerges also, as stated before, by inference or as approximation from earlier hydrodynamic work. As regards experimental evidence, a good linear relationship between slope and $[\eta]^2$ has been repeatedly reported whenever $[\eta]$ changed with the molecular weight in a polymer-homolog series. This will again be confirmed below. However, as soon, as k' varies for one and the same polymer fraction on account of a change in the solvent, we are left without any clear-cut relationship. Several attempts have been made to calculate this function on the basis of a physical model involving the changes in intermolecular forces from one solvent to the other (20,20a). They have not met with conspicuous success, and one can see that as long as the intrinsic viscosity itself cannot be calculated as a function of the solvent the calculation of the slopes is

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viscosity in that solvent. For polystyrene, benzene and methyl ethyl ketone, we obtain the following ζ's and k's.

$$\frac{\zeta_{\varphi}\eta_{MEK}}{\zeta_{MEK}\eta_{\varphi}} = 0.23 \qquad \text{and} \qquad \frac{k'_{\varphi}}{k'_{MEK}} = 0.5$$

it should be noted that these two ratios are appreciably different, so that the participation of additional factors must be suspected. We will return to this later in the text.

without proper basis. In view of this it seems of advantage to look into the experimental evidence for the influences that come conceivably into play in concentration effects.

INITIAL SLOPES OF η_{sp}/c vs. c CURVES

Any analysis of slopes,[1] since it cannot yet be brought onto an absolute basis, has to be carried out by comparison. As a suitable standard of reference we propose the behavior of spheres, for which the mechanism of the early hydrodynamic interaction is fairly well understood and the theory has given adequate results.

We begin by plotting the slopes against squared intrinsic viscosities of some fractions, e.g., of methyl methacrylate and of polystyrene-methyl methacrylate copolymer, in toluene and in methyl ethyl ketone, (Fig. 1). They have been recently measured by Kapur (21) over a wide range, but at the same time they are representative of most measurements reported in the literature in that, apart from a statistical scattering, the slopes fall on straight lines if plotted against $[\eta]^2$. The ratio of slopes to $[\eta]^2$ in Fig. 1 gives k' values which fall within the usual range (ca. 0.5). If we enter the corresponding values for spheres, i.e., $[\eta]^2 = 0.000625\ \rho^2$ (ρ equals particle density),

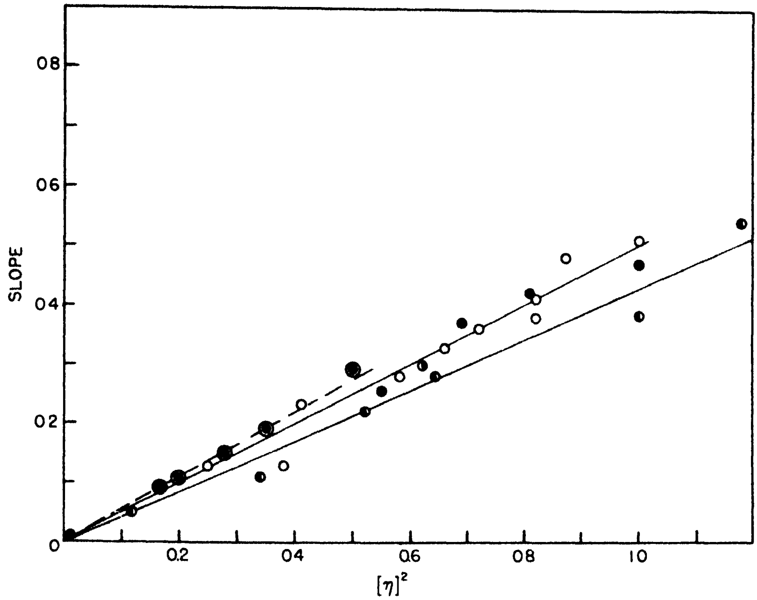

Fig. 1. "Slopes" (η_{sp}/c vs. c curves) vs. $[\eta]^2$ of polymethyl methacrylate and of methyl methacrylate-styrene copolymer fractions in toluene and methyl ethyl ketone: polymethyl methacrylate in toluene (●), in MEK (○); methyl methacrylate-styrene in toluene (◐), in MEK (●); rigid spheres (●).

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[1] In order to avoid misunderstandings, we shall in this paper mean by "slope" always the initial slope of the linear plot of η_{sp}/c vs. c, as mentioned above. The slopes of "slopes" vs. $[\eta]^2$ will be referred to as k'.

slope = 0.00141,[1] and k' = 2.25, we find this point near the origin, but considerably above the extrapolation of the lines toward zero, (cross in Fig. 1; see also enlarged inset in Fig. 3). This point could lie on the extrapolated lines only if the monomer unit would be a sphere itself. Our attention is thus drawn to the fact that for a number of polymer homologue series there will be already in the monomer-to-low-polymer range a number of slopes belonging to the same intrinsic viscosity, or a number of intrinsic viscosities for a particular value of slope. Of course, this is due to the very variations in structure, to account for which the k' factors have been introduced in the past. We shall, however, be in a better position to obtain some insight into the nature of k' as a function of the structure if we begin with the monomer, especially if we assume it first to be spherical.

The main clues come from Taylor's (22) calculation or the viscosity of suspensions of liquid spheres, and from one of the authors' (23) work with models. The former shows that the specific viscosity falls with the shear strength or viscosity of the suspended liquid, from the value 2.5 in the case of complete rigidity, to below 2 for a viscosity equal to that of the medium. It may drop lower still if the solute droplets are easily deformed or divided. A similar decrease in specific viscosities was found for various shapes, rodlets, curls, rings, nets, platelets, if they lost their rigidity by softening. At the same time the slopes decreased and dropped comparatively more than $[\eta]^2$, so that k' decreased. Only a few such cases have been investigated, but the drop in k' was found every time, and may be assumed to be the rule. Figure 2, showing the η_{sp}/c vs. c curves, illustrates this behavior. We learn from this that internal softness of particles is not only a reason for lowering the intrinsic viscosities but even more so for lowering the slopes.

Returning to the rigid spheres, their k' of approximately 2 obviously represents the highest value for the slopes of the series of spheres of increasing rigidity (cross, Figure 3), which is the only parameter that can be altered with spheres (for our present purpose, porosity can also be considered as internal softness). Increase in radius leaves all spheres geometrically similar and does not change the viscosity-concentration (vol. fract.) relation. Let us now join two spheres, or take an ellipsoid of the same short axis and a = 2r, and after this a third sphere, or an ellipsoid with a = 3r, and so forth. We change thereby the shape and will expect a different type or degree of interaction, i.e., we will have a change in k'. Our model experiments permitted us to follow this change, though not with a high accuracy. We found that at first k' increased very rapidly with increasing axis ratio, then less, and finally reached an almost constant value (approx. 6). Rather surprisingly, the plot of slope vs. $[\eta]^2$ gives again a straight line, or very nearly so (Fig. 3). These two features together necessitate that the straight line cannot pass through the origin. As a matter of fact, it terminates in the point for spheres which, apart from the linearity of the extrapolation, is not surprising. This linearity in the face of changing geometry may be reconciled by the formal possibility stated above, of replacing rodlets by effective spheres of action.

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[1] This value is based on a coefficient of 14.1 as calculated by Guth, Simha, and Gold, in agreement with model experiments in a Couette apparatus. The same models in capillary viscometers give lower values, corresponding to a coefficient 8-10. As shown later, an approximate recalculation along a new approach gives also a value of 10. Whatever the final check on the theory will be, the following arguments are not based on any particular value.

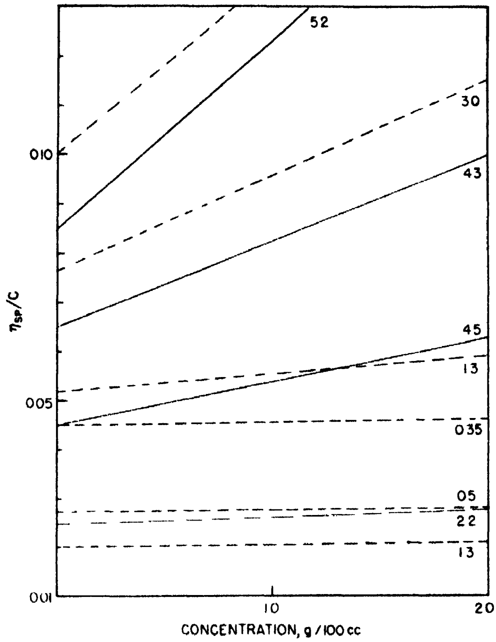

Fig. 2. η_{sp}/c vs. c curves for particles of various shapes and consistencies. Solid lines for rigid particles; broken lines for flexible particles. The numbers at the lines give the k′ values: ——2.2 spheres; ——4.5 rodlets, axis ratio 1:5; —— 4.3 rodlets, axis ratio 1:17; ——5.2 rodlets, axis ratio 1:23; ---- 1.3 emulsion (o-toluidine-water); ---- 0.5 very soft threads, axis ratio 1:20; ---- 0.35 soft threads, axis ratio 1:14; ---- 1.3 flexible rodlets, axis ratio 1:20; ---- 3.0 flexible rodlets, axis ratio 1:60.

For the next step we remember that any rodlets, if softened, exhibit a less steep slope and a smaller k'; it shows that apart from the one linear function for rigid rods, there is probably a family of presumably straight lines, with slopes decreasing according to the rodlets' softness, and leading into the points of spheres of equal consistency. Further, we find a similar behavior if a chain remains rigid but becomes increasingly kinked, or if a chain is looped to a ring; see also Kramers' calculations (24). Kinking, looping, and softening together superimpose to cause a still further drop in the k' values of polymers.

These features may be summed up in a tentative statement of the following regularities: all geometrically similar shapes of suspended particles exert the same type of interaction[1] (though Guth's calculations show that for spheres this is less rigorously true than the independence of the intrinsic viscosity on particle size); with the geometry and consistency the interaction changes, but if the geometry is altered slowly and in a regular, definite way (extension of rods, plates, rings, coils, etc.) the proportionality of the slopes with $[\eta]^2$ may be approximately maintained. Depending on whether the straight part of this function intersects at the origin or not, k' may remain constant throughout. Even if not, the angle between the linear part and connecting lines from its points to the origin may become so small as to keep k' practically constant. Expressed differently, on further additions of, for example, links to an already long chain, the deviation from geometrical similarity becomes insignificant.

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[1] Provided the same degree of Brownian movement.

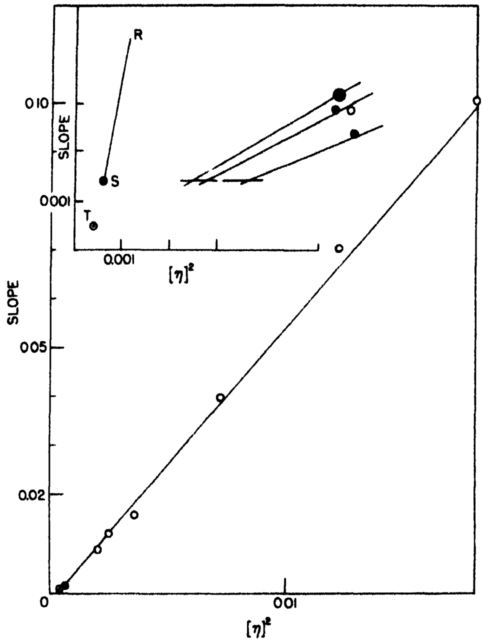


Fig. 3. "Slopes" (of η_{sp}/c vs. c curves) vs. $[\eta]^2$ of rigid rods of increasing axis ratio (1:5 to 1:32) in model suspensions (measurements in Couette viscometer at low rates of shear). Inset shows range near origin on larger scale. Line R is the extension of the lines of the rods. It terminates at S, the point for spheres; T is the point for the toluidine emulsion. The 3 other lines represent the extrapolation of those in Figure 1.

INTERACTION AND SOLVENT EFFECTS (25,26)

It will be seen that this behavior is in agreement with Huggins' assumption that k', introduced to correct for deviations of a chain segment from Stokes' law, will hold for any additional segment in a chain and thus remain independent of the molecular weight. But now we are able to give an explanation also for the solvent effect. We have stated before that proportionality with $[\eta]^2$ is generally experimentally established and theoretically intelligible: if, namely, all the characteristics of a suspended particle which contribute to the distortion of flow can be expressed by the intrinsic viscosity as a volume per weight, then, if these volumes overlap, any interaction should be approximately multiplicative, i.e., be proportional to $[\eta]^2$.

The proportionality factor will, however, depend on more than the mere volume, namely, also on the structure of the disturbed range. Hydrodynamically, this will come in by considering the boundary conditions at the surface, and the damping inside the effective volume. The greater the surface area and the greater the damping of any velocity, the greater will be the interaction per volume or intrinsic viscosity. It follows that Huggins' procedure is incomplete and that the coefficient of c^2 cannot be defined by the intrinsic viscosity and a Stokes' correction factor, but must contain a further interaction factor characteristic for each system.

Actually one type of hydrodynamic interaction will take place intramolecularly. It arises from segments of the same chain being situated closely enough so as to overlap in their individual effects on the flow of the surrounding solvent. This intramolecular close approach is often called back-coiling, and its effect might be expressed by an additional correction factor for a Stokes' type of interaction. This factor will also contribute to the intrinsic viscosity and, where changing conditions are such as to leave the amount of back-coiling constant, as presumably in adding links to an already long chain, will remain constant. On the other hand, if the intramolecular potentials and distances change as, for example, with the solvent, the factor will change. It will be seen that this influence of the solvent is supplementary to the one proposed by Alfrey, Bartovics, and Mark (19).

How the intramolecular distances affect intermolecular interaction beyond the proportionality with $[\eta]^2$ can be seen qualitatively in the following way.[1] Intermolecular interaction consists basically in the disturbance of flow created by a first particle, being "reflected" by another particle and acting back on the originator. The process is of course mutual and results in a greater interference with free flow. If the reflecting particle is not rigid, the reflection is reduced and the disturbance of the first particle can be partially dissipated inside the second. This superimposed internal flow will depend on the distances and on the relative mobility of the units that are linked together to form a polymer particle. The more solvent there is inside, the easier for the disturbance to penetrate. Again, for the same average distance much will depend on whether the units can move, or are fixed relative to each other or in relation to the coil boundary. One can see that the extent of interaction will be largely decided by what might be termed a particle opacity to flow superimposed by the presence of other particles, just as the intrinsic viscosity is determined by a similar opacity or resistance to flow of volume elements in the solution. To a certain extent these opacities will be connected, but will oppose the effects of changes in the axis ratio of one and the same particle. The more the longest dimension and the intrinsic viscosity of a coil increase on stretching, the more will its effectiveness of "reflection" decrease. Unless, therefore, the molecular opacity can be described as a function of the intrinsic viscosity, the concentration equation in any one solvent will not be predictable from a knowledge of intrinsic viscosities and k' factors in other solvents, and the ratios of ζ's and k's cannot be the same.

[1] We apply here the arguments of Guth and Simha (15).

A plausible explanation of the changes of k' with solvent follows immediately. If a coil of molecular chain is brought isothermally from a poorer solvent, where van der Wall's forces prevent a random configuration (incomplete intramolecular evaporation) to an ideal one where the coil extends, the decrease in density and a probably accompanying increase in internal flexibility will place the particle in a different category, not so much as regards the Stokes' correction part of k', which will change only if there is a change in solvent resistance, but mainly as regards the interaction part of k'.

The resultant changes in slope and k' can be easily symbolized graphically (Fig. 4). Imagine a given slope represented by a point X belonging to a $[\eta]^2$ value in a series of fractions. On increasing the axis ratio in the better solvent, the point would move upwards with the intrinsic viscosity, say to Y, but on account of the internal loosening will simultaneously drop to the appropriate lower proportionality, say to Z. This is equivalent to an increase in slope and a decrease in k'.

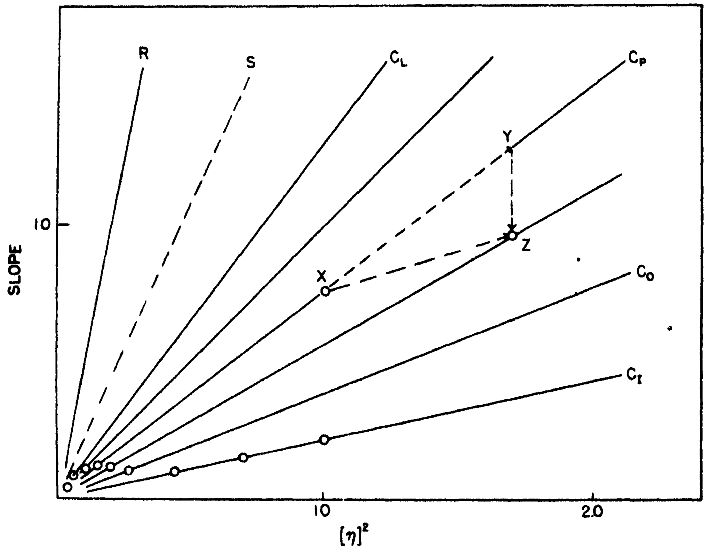
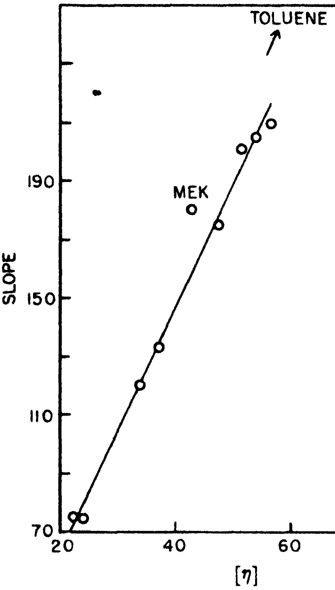


Fig. 4. 'Slopes" (of η_{sp}/c vs. c curves) vs. $[\eta]^2$. R, model experiments with rigid rods, extrapolated. S, hypothetical line for spheres, extended. C_L to C_I, generalized lines for a polymer in six solvents, varying from the lowest solubility C_L, over poor solubility C_p, and optimal solubility C_o in a solvating system, to ideal solubility C_I. The curve indicated by the points at the low left-hand corner shows changes in k′ with molecular weight, to be expected in the monomer-to-low-polymer range in an ideal solution.

Sometimes the drop may become so great that the slope stays practically constant. In such cases k' would be proportional to $1/[\eta]^2$. Mostly, though, k' is found to be more nearly proportional to $1/[\eta]$, i.e., the slopes in different solvents will give a better straight line if plotted against $[\eta]$ instead of $[\eta]^2$. This is illustrated in Figure 5 and 6, where the slopes of polystyrene and vinylacetate are plotted against intrinsic viscosities in a wide range of solvents (27,28).

The whole argument can, of course, be taken in reverse, i.e., when the coiling up leaves the particle denser and more rigid, possibly also on account of more internal contacts and of forming temporary loops.

It is interesting to note, though, that when this increase in density and stiffening has reached a certain degree, the particles usually aggregate and precipitate. This occurs for the same polymer fraction always at the same intrinsic viscosity, regardless of the nature of the solvent (precipitant), and also at the same k', as a rule for values between 0.8 and 1.3. These k'-values are still below those of rigid or compact particles (e.g., phenol resins 1.5, rigid spheres 1.7-2.2). It indicates that solubility is lost when the individual chain segments begin to cluster to a definite degree and to form permanent contacts, while still retaining an appreciable amount of solvent. k' values above 2 will belong to more-or-less rigid and extended bodies. Still higher values, above about k' = 6, ought to be due to two-dimensionally extended particles, i.e., platelets or flakes. In fact, in some soap solutions (flat micelles) k' values as high as 10 have been reported (29).



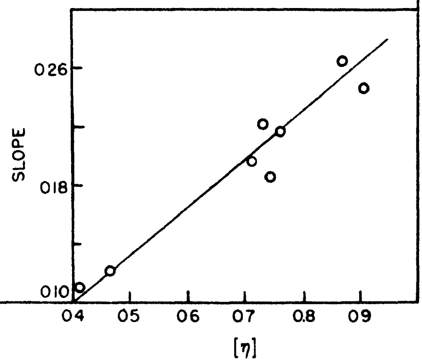


Fig. 5. "Slopes" (of η_{sp}/c vs. c curves) vs. [η]. Very high molecular weight polystyrene, in mixtures of acetone and methylcyclohexane from 15:85 to 75:25 (precipitation points at 12:88 and 78:22, maximum viscosity at 42:58).

Fig. 6. "Slopes" (of η_{sp}/c vs. c curves) vs. [η]. Polyvinyl acetate (M.W. 90,000) in solvents ranging from $\mu = 0.38$ to $\mu = 0.51$.

It will be seen that if in a series of homologs the particles change from a spheroid to a short rod, then to a kinked short chain, to a long and flexible chain, and eventually to a coil, k' will undergo complex changes on account of the changing interaction, where it might have changed little as hydrodynamic (Stokes') correction factor. The possible course of these changes is indicated in Figure 4 (circles).

Finally, as regards the influence of temperature, it should be pointed out that most of the phenomena here considered are relative, and affected by temperature in like manner. Consequently, most temperature effects (including the variation of k') are small, unless they are due to altered particle solubility and not complicated by changes in the degree of orientation.

In concluding this section we may remark that the picture here developed is undoubtedly still crude and incomplete. Yet it seems to us to focus attention to some aspects of k', as the first interaction constant, which have so far been neglected to the detriment of the further progress of understanding. Only after the approach presented here will have been put on a more quantitative basis, will it be possible to introduce hydrodynamic considerations and refinements profitably. Questions of interparticle contacts and associations will have to be investigated after this. It may be presumed that they will, as incipient effects, contribute to the magnitude and structure of the cubic term; where they become a more pronounced phenomenon a completely different approach will have to be found.

A NEW APPROACH TO THE FIRST INTERACTION COEFFICIENT OF SPHERES

Throughout this discussion it has become more and more obvious that the effect of concentration on the viscosity of a system of separate particles is, in many respects, analogous to that encountered in the treatment of intrinsic viscosities of flexible long-chain molecules. In both cases the deviations from additivity are due to the interactions between the elements making up the dispersed system. Thus, in the case of concentration effects (where rigid particles are concerned), one encounters changes in the fluid velocity due to hydrodynamical particle-particle interaction, whereas in the rigorous treatment of intrinsic viscosity of long-chain molecules one again encounters such velocity changes (although the effects are limited to a smaller region of space) because of the hydrodynamic interactions of the elements making up the chain. Where the concentration effect for solutions of polymer molecules is concerned, one has a combination of the two types of interaction mentioned above, intra and interparticle reaction. Significant differences between these two types of problems arise, however, because of the presence and absence of constraints limiting the positions of the interacting elements in the case of intrinsic viscosity as compared to concentration dependence. The existing constraints are especially important when one comes to a quantitative consideration of these problems. Another important difference refers to what is often termed "inter-twining" of polymer chains.

In general, mathematical physics has not been able to treat cases where multiple interaction leads to what can be classed under concentration effects. In the few cases where such treatments have been made with some success, it has been necessary to sacrifice rigor, making simplifying assumptions and adapting particular models. During the past year, in connection with the intrinsic viscosity of high polymers, two treatments have appeared, taking account of interactions between the chain elements. In one of these, by Debye and Bueche (8), a simplified model is adopted in which the polymer molecule is represented as a system of point forces contained in a porous sphere of diameter equal to the root-mean square length of the polymer. The distribution of point forces (representing the chain elements) is assumed to be uniform, and the effect of the point forces is to modify the fluid flow. The modification of flow is then achieved by including these forces in the usual hydrodynamic equation of equilibrium. In this way, the almost infinite set of boundary conditions which would be needed to solve the usual hydrodynamic equations is dispensed with. The resulting problem is then the relatively simple one of solving two partial differential equations, that for within the molecular sphere and that for outside the sphere (usual hydrodynamic equation), and adjusting the constants so that the velocities and stresses across the molecular sphere are the same (permeable sphere). A calculation of the dissipated energy then completes the problem.

In the second method of treatment, that of Kirkwood and Riseman (7) (K.R.), instead of simplifying the model, a statistical treatment with an assumption regarding the size of a fluctuation about a mean density is made. Thus, in this treatment, the modern conception of a polymer molecule as a flexible chain of elements is retained. The effect of retaining this model appears in that the mathematical treatment becomes more complex with the appearance of an integral equation containing a singular kernel. The mutual influence of the chain elements in affecting the flow pattern is taken directly into account, with the calculation of an average perturbation of the fluid velocity. The average being taken over all configurations of the flexible chain. In this respect, the method becomes, in principle, directly applicable to the calculation of concentration effects. However, the lack of constraints, such as are present between the elements of a single chain, makes the resultant problem so much more difficult. Though lacking the rigor of the K.R. method, the D.B. method may lend itself better to estimating the concentration dependence of such hydrodynamic quantities as viscosity and frictional resistance of a particle.

Looking back to the D.B. treatment, if the size of the molecular sphere is increased indefinitely, we have exactly the case of a solution of particles, whose concentration depends on the density distribution of the particles. The hydrodynamic effect of each particle has been assumed to be replaceable by a point force acting on the fluid. The resultant action of all three forces, then, should yield the flow pattern, as affected by the mutual interactions of the actual particles. A particular particle in such a system will have, relative to itself, a flow pattern due to the action of the density distribution of point sources of force, plus that due to the usual boundary conditions of no slippage at the particle surface. The above is equivalent to regarding, from a hydrodynamic viewpoint, that the concentrated solution is a "new liquid" whose equations of equilibrium differ from the usual by the inclusion of "damping forces" due to the distribution of point sources. A particle in such a "new liquid" upon which we focus our attention will then be subject to the usual boundary conditions.

Bueche and Brinkman (30) have independently used this method of replacing the large number of particles in a concentrated solution by such a system of forces, and have thus extended the Stokes problem to the case of higher concentrations. The method of calculation is exactly the same as for the single particle problem, except that the modified hydrodynamic equation is used. In applying this method to calculate the frictional resistance of a long chain molecule, Bueche has again, following Debye, represented the polymer molecule by a molecular sphere containing the chain elements distributed uniformly. The other polymer molecules in the solution are again replaced by point forces. The modified hydrodynamic equations, relating to the flow inside and outside the molecular sphere therefore contain two different coefficients, relating to the frictional resistance of the chain as a whole. Using similar considerations one should be able to calculate the viscosity of a concentrated solution of high polymers.

The accuracy of such a calculation would depend on the general assumption made in the replacement of the boundary conditions by a set of point forces, and in addition the assumption inherent in the intrinsic viscosity theory of replacing the actual polymer molecule by a hypothetical molecular sphere containing a uniform distribution of chain elements.

The treatment of the effect of a particle in perturbing the flow lines of the fluid by replacing the actual particle by a point force is not new. Thus Burgers (9), using Oseen's method, made a large number of hydrodynamic calculations, obtaining the change in the fluid velocity by regarding the particle as replaced by a point force acting upon a fluid element at some distance from it. However, it is physically obvious that the fluid velocity so obtained cannot be better than an approximation, the approximation becoming successively worse as the distance to the surface of the particle is approached. Thus, in the replacement of the large number of particles by a system of point forces, one must of necessity accept the fact that the true boundary conditions at the particle surface can no longer be obtained.

Furthermore, when the particles under consideration are of large size relative to the molecular dimensions of the solvent the question arises whether the influence of the particle can be represented simply by a force, or if, rather, a system of forces and moments are necessary to yield an adequate description. Where the particles are small (i.e., elements of a polymer chain) the necessity for such a representation is obviated. Thus, where large particles are concerned the treatment by replacing by a simple force system may be just a first-order approximation to the concentration effect.

To sum up, the Debye treatment may be considered to offer essentially a first-order approach to the hydrodynamic problem of concentration dependence and, in addition, should not be used for the entire concentration range.

Insofar as the Debye method may allow for the treatment of concentration effects, and with the view to a possible future application in the realm of concentrated polymer solutions (at least in the region of not-too-high concentration) we have started to apply this method to the calculation of the second term in the Einstein viscosity formula. For this purpose the two treatments–that of Einstein and Debye–have been combined. With Einstein, we consider the general motion of the fluid to be made up of translatory, rotatory, and shearing parts. The particles in the fluid will partake of the first two motions but will act so as to modify the third. Under these circumstances the particles, of which there are n per cc., can be considered as fixed in a fluid whose motion consists only of the dilatory component. Considering any arbitrary particle, the flow relative to it is then described by the inclusion of a damping term, due to the forces exerted on the fluid by the presence of all of the other particles in the fluid. In the limit $n \rightarrow 0$ this problem reduced to just that of Einstein. The solution of the hydrodynamic equations lead to velocities which contain factors $e^{-\gamma r}$ similar to those obtained in the Debye viscosity theory, and which indicate a very rapid decrease of liquid velocity. In addition, the coefficients arising from the boundary conditions change from those in Einstein's case in the following manner:

$$A_1 = -5/6\ A_0 P^3 A_\gamma \qquad B_1 = -\ A_0/6\ P^5(1 - \beta_\gamma)$$

$$A_2 = -5/6\ B_0 P^3 A_\gamma \qquad B_2 = -\ B_0/6\ P^5(1 - \beta_\gamma)$$

$$A_3 = -5/6\ C_0 P^3 A_\gamma \qquad B_3 = -\ C_0/6\ P^5(1 - \beta_\gamma)$$

where P = radius of particle and A_0, B_0, C_0 are constants describing the original flow:

$$u = A_0 x \qquad v = B_0 y \qquad w = C_0 z$$

$$A_\gamma = \frac{e^{\gamma P}}{1 + \gamma P} \qquad B_\gamma = \frac{5}{1 + \gamma}\left\{1 + \frac{P_\gamma}{3} + \frac{2}{(P\gamma)^2}\left(1 + P\gamma - e^{\gamma P}\right)\right\}$$

We note that in the limit n→0 these constants became identical with those of Einstein.

If these constants are used in Einstein equations, to which the above equations reduce in the limit, we obtain instead of the Einstein results the following:

(1) Energy dissipated per unit volume:

$$W = 2\delta^2(1 + A_\gamma\varphi/2)$$

$$\delta^2 = A_0^2 + B_0^2 + C_0^2$$

$$\varphi = \text{Volume fraction of particles}$$

(2) For the values of the principal dilations of the motion:

$$A^* = A_0(1 - A_\gamma\varphi)$$

$$\delta^{2*} = \delta^2(1 - A_\gamma\varphi)^2$$

(3) For the viscosity:

$$\eta^* = 1 + 5/2\ A_\gamma\varphi + 4A_\gamma^2\varphi^2$$

taking for f, Stokes values of $6\pi\eta P$:

$$A_\gamma^2 = 1 + \frac{9}{2}\varphi + \frac{81}{16}\varphi^2$$

$$\eta^* = 1 + 2.5\varphi + 10.6\varphi^2$$

It should be emphasized that the values obtained here are approximate. An exact calculation for the dissipated energy will be made in the near future so that we may be able to compare the viscosity obtained using the Debye method with that resulting from experiment.

It may, however, be taken as an encouraging sign of moving in the right direction, that a reasonable result is obtained at the first approach. In view of the importance of the viscosity-concentration problem and the difficulties involved, the availability of an additional possible avenue is quite important.

CONCLUSIONS

It will be appreciated that, as stated in the beginning, our remarks are not so much intended as a final contribution, but rather as an attempt to stimulate further progress in the field. With this in view controversial points were not avoided but on the contrary emphasized. Nor is it claimed that we have touched all the possible issues; rather we have concentrated on those which we feel have been so far neglected and should now come under proper review. Notwithstanding these reservations the following points seem to us worth reporting even at this early stage:

1. k' as introduced by Huggins is not sufficiently defined to form a part of the first interaction coefficient.
2. Most workers so far concerned with k' have attempted to endow it with a physical significance which was incompatible with the original definition.
3. Any redefinition will have to take into account that, instead of containing a correction factor for the hydrodynamic effectiveness of a chain element which answers the definition by Huggins, the coefficient of the square term in the concentration has to include at least one interaction factor which must be a function of the molecular state in solution and does not enter into the linear term, i.e., into the intrinsic viscosity.
4. One of the variables of the molecular state determining k' must be the internal mobility of dissolved or suspended particle, another one, not necessarily connected, will be its density within the volume taken up.
5. It appears that for a given series of polymer homologs these properties are independent of changes in the molecular weight, i.e., amount approximately to a constant factor. They have, however, to be expressed by a factor roughly inversely proportional to $|\eta|$ whenever the solvent changes.
6. k' appears consequently as a potential measure of the internal deformability of a particle and its resistance to solvent penetration.
7. From the method used by Kirkwood and Riseman, and by Debye and Bueche, to calculate intrinsic viscosities from the hydrodynamic interaction of individual segments, it seems possible to calculate concentration effects in solution. Such an attempt is reported and preliminary results for spheres are quoted.

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Synopsis

During recent years attempts have been made to formulate a viscosity-concentration relationship. The method of Huggins, in introducing a factor k' as a hydrodynamic correction factor is examined, and in particular the attempts to draw conclusions relating k' to the thermodynamic properties of the solution. An explanation is offered to correlate the experimental viscosity-concentration relationship and the change of solvent. A possible method for the actual calculation of concentration effects has been applied to the case of a suspension of spherical particles, for which, as a first approximation, a value of 10.6 for the coefficient of the c^2 term has been obtained.

Résumé

Au cours de ces dernières années, des essais ont été faits en vue de formuler une relation entre la viscosité et la concentration des solutions. La méthode de Huggins, qui introduit un facteur k' comme correctif hydrodynamique, est examiné, particulièrement quant aux conclusions qui relient k' aux propriétés thermodynamiques de la solution. Les auteurs présentent une explication, établissant une relation entre les valeurs expérimentales de la viscosité et de la

concentration d'une part; et le changement de solvant d'autre part. Une méthode possible pour calculer actuellement les effets de la concentration, a été appliquée dans le cas d'une suspension de particules sphériques, pour lesquelles, en première approximation, une valeur de 10.6 a été obtenue pour le coëfficient affectant la concentration au carré (c^2).

Zusammenfassung

In den letzten Jahren wurden Versuche unternommen, das Verhaeltnis zwischen Viskositaet und Konzentration zu bestimmen. Die Huggins'sche Methode, in der ein Faktor k' als hydronamischer Korrektionsfaktor benuetzt wird, und besonders Versuche, von k' Rueckschluesse auf die thermodynamischen Eigenschaften der Loesung zu ziehen werden kritisch untersucht. Eine Erklaerung der gegenseitigen Abhaengigkeit des benuetzten Loesemittels und des experimentalen Verhaeltnisses zwischen Viskositaet und Konzentration wird vorgeschlagen. Eine moegliche Methode fuer das Berechnen der Konzentrationswirkungen wurde auf den Fall einer Suspension kugelfoermiger Teilchen angewandt, wo als erste Anaeherung der Wert 10.6 fuer dem Koeffizienten des c^2 Terms erhalten wird.

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Dependence of Tensile Strength of Vulcanized Rubber on Degree of Cross-Linking*

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INTRODUCTION

The suitability of disazodicarboxylates as quantitative cross-linking agents for the preparation of rubber vulcanizates of known degrees of cross-linking has been emphasized previously (1,2). In a recent paper (2) we have presented the results of an investigation on the dependence of the equilibrium force of retraction on the elongation and degree of cross-linking of rubber and GR-S vulcanized with these compounds. The present paper reports an extension of these investigations of the relationship of physical properties of rubberlike materials to their network structure. Specifically, the tensile strength of azo vulcanized natural rubber has been explored as a function of the degree of cross-linking and of the extent of modification of the chain units.

The tensile strengths of natural rubber specimens vulcanized to various extents using sulfur alone or sulfur in conjunction with various accelerators have been investigated in considerable detail recently by Gee (3) who has emphasized the critical dependence of the tensile strength on the degree of cross-linking. Values for the latter quantity, however, were deduced indirectly from the equilibrium force of retraction using the simple proportionality relationship between force of retraction and degree of cross-linking afforded by the theory of rubber elasticity. This relationship is known to be only approximately valid (2). Furthermore, the effects on the force of retraction of chain scission, which doubtless accompanied some of the vulcanizations to a considerable degree, were disregarded. For these reasons, Gee's values for the degrees of cross-linking occurring in his vulcanizates are only approximate estimates, and in a few cases they may be seriously in error. Nevertheless, the general character of the relationship between tensile strength and degree of cross-linking which he obtained is confirmed by our results on rubber samples quantitatively cross-linked with measured proportions of decamethylene-dis-methyl azodicarboxylate.

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EXPERIMENTAL

Materials

The rubber designated as "high molecular weight" consisted of pale crepe which had been subjected to 15 passes between mill rolls. The intrinsic viscosity of this rubber in toluene at 30° was 5.5, which corresponds to a viscosity average molecular weight of about 1.1×10^6 according to the relationship established by Carter, Scott and Magat (4). The "low molecular weight" rubber was obtained by mastication of pale crepe for 20 minutes on a cold mill with close set rolls. Its intrinsic viscosity in toluene at 30° was 1.64, corresponding to a viscosity average molecular weight of about 175,000. Number average molecular weights of the two rubbers presumably were about 500,000 and 100,000, respectively.

Stock solutions in benzene were prepared and stored in darkness. To obtain the proper consistency for the preparation of films, concentrations of about 5% and 10% were chosen for the high and low molecular weight materials, respectively.

Pure decamethylene-dis-methyl azodicarboxylate (referred to as "10-1") was used exclusively as the cross-linking agent. It was prepared and purified as previously described (1,2). In some of the experiments the analogous monofunctional azo compound, ethyl azodicarboxylate (referred to as EAD), was used for the purpose of similarly modifying some of the polymer chain units without introducing cross-linkages. This substance was prepared by the method of Ingold and Weaver (5).

Preparation of Vulcanizates

The 10-1 disazo compound dissolved in benzene was mixed with the stock solution of rubber in precisely the required proportion and films were cast on glass plates in the manner previously described (2). It was found advantageous, however, to use a large sheet to plate glass without barriers to confine the viscous solution, the thickness being controlled merely by the rate of drying after pouring the solution onto the plate. The plate was leveled and heated uniformly at 60° for two hours and the vulcanized sheet removed. Thicknesses of different sheets varied from about 3 to 11 mils (thousandths of an inch), but generally were in the vicinity of 5 mils.

In agreement with the indications of the force of retraction measurements (2), heating at this temperature for two hours was adequate for completion of the cross-linking reaction; no significant change in tensile strength was observed when samples were heated for longer periods and, in fact, little change in either tensile strength or elongation was noted when the heating period was reduced to one hour.

Determination of Tensile Strength

A diagram of the apparatus employed for the determination of the tensile strength is shown in Figure 1. The method whereby the load is applied by continuous addition of a liquid, in this case water, to a container supported by the sample, is a variation of similar schemes previously applied on various occasions to tensile tests on rubber and on fibers.

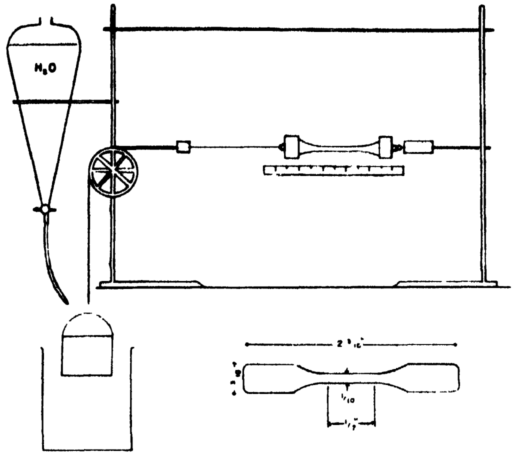

Fig. 1. Schematic diagram of the apparatus used for tensile strength determinations. The dimensions of the test dumbbells are shown in enlarged scale at the lower right.

Dumbbell specimens of the dimensions shown were cut from the sheets. Their thicknesses were measured at intervals over the constricted portion using a thickness gage having a dial divided in 0.1 mil units; interpolations to 0.05 mil appeared to be valid. Samples showing appreciable variation of thickness over the mid section of the dumbbell were discarded. Weights of rectangular strips cut from the mid sections of several dumbbells confirmed the accuracy of the thicknesses determined in the above manner. A pair of ink marks exactly one-half inch apart was placed within the uniform section of the dumbbell.

The dumbbells were fastened between small clamps, each consisting merely of a pair of aluminum plates on the faces of which thin strips of vulcanized rubber were cemented. The end of the test specimen was placed between the rubber covered surfaces of the plates, which were then fastened to one another with a pair of screws running through the plates. The clamp at one end of the sample was anchored in fixed position while the clamp attached to the other end was connected to a fine copper wire which passed over the pulley and to a hook from which a pail could be suspended, as shown in Figure 1. The pulley was pivoted with a ball bearing of very low friction. In carrying out a determination, the empty pail was attached and gradually lowered until its weight was borne by the sample. Water was then allowed to flow into the pail at a constant rate while a second operator observed the distance between the marks with a ruler. The length at the instant rupture occurred was recorded and the pail and water it contained were weighed. The tensile strength in pounds per square inch initial cross section was computed directly. The elongation, expressed as percent increase in length over the initial length, was obtained in rough approximation only. Tests in which the sample broke at a point appreciably outside the region of uniform section were discarded. Such instances were rare.

TABLE I. Sample Tensile Strength Data for Two Test Sheets of the Same Cure (0.30 Equivalent % 10-1)

Sheet No. 1		Sheet No. 2	
Thickness of test piece, mils	Tensile strength, p.s.i.	Thickness of test piece, mils	Tensile strength, p.s.i.
4.5	1880	3.85	1920
4.9	1970	4.75	2200
4.5	2140	5.15	2290
2.7	2200	5.35	2310
3.0	2290	5.6	2350
4.35	2340	5.7	2390
5.4	2490	4.8	2410
4.9	2520	5.55	2560
5.25	2630		
Mean	2278	Mean	2304
Av. deviation from mean	±200	Av. deviation from mean	±113

RESULTS

Typical results are given in Tables I and II. The former table contains tensile strengths obtained from two sheets separately prepared using the same proportion of the cross-linking agent, namely 0.30 "equivalent percent" of 10-1; in other words, the proportion of the disazo compound employed was sufficient to react with 0.30% of the C_5H_8 units in the rubber (i.e., 0.15 mole of 10-1 per 68 g. of rubber).[1] In Table II are given the results of individual tests on vulcanizates prepared with 1.00 and 3.00 equivalent percent of 10-1. In each of these tables the tensile strengths for a given set are arranged in increasing order. Although the tensile strengths are recorded to the third significant figure, errors of 15 to 50 p.s.i. in the individual determinations are introduced by uncertainties in the sample thicknesses alone.

The results obtained with different sheets prepared using the same proportion of the vulcanizing agent were found to be in good agreement, as is the case for the instance shown in Table I. Hence, results from two or more sheets of the same cure are not differentiated in subsequent tables. Examination of Tables I and II shows that variations in thickness are unimportant. In subsequent tables the thickness of the test piece has not been recorded. As stated above, however, test sheets usually were close to 5 mils in thickness.

Principal results of tensile tests on the high molecular weight rubber are summarized in Table III. In most instances, two or more separate sheets were vulcanized with the same proportion of 10-1 and test samples were taken from each of them. Results obtained on high molecular weight rubber vulcanized with 10-1 and modified with EAD (ethyl azodicarboxylate) are similarly presented in Table IV. Data shown for zero percentages of EAD have been taken from Table III. Table V presents the tensile results for the low molecular weight rubber vulcanized with various proportions of 10-1. Average deviations from the mean and root-mean-square deviations (or standard deviations) σ are given in the last two columns, respectively, of Tables III, IV and V.

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[1] The "equivalent percentages" used throughout this paper correspond to ρ x 100 of the earlier paper (2).

TABLE II. Sample Tensile Strength Data for Two Different Cures

Thickness, mils	T.S., p.s.i.	Thickness, mils	T.S., p.s.i.	Thickness, mils	T.S., p.s.i.
		1.00 Equivalent % of 10-1			
9.4	2520	5.3	3060	5.45	3190
9.4	2560	6.4	3070	11.4	3210
5.9	2600	5.15	3080	5.75	3240
10.3	2710	5.8	3090	5.5	3270
4.6	2740	10.2	3100	7.3	3280
4.35	2820	9.9	3120	5.1	3320
4.5	2960	5.15	3120	5.5	3360
5.0	2990	4.45	3140	5.25	3430
3.85	3000	4.9	3140	5.15	3500
10.6	3000	8.2	3160	5.25	3660
5.75	3060	7.8	3180	7.4	3680

Average deviation from mean: ±200 p.s.i.

Ultimate elongation: 680 ± 15%

Thickness, mils	T.S., p.s.i.	Thickness, mils	T.S., p.s.i.	Thickness, mils	T.S., p.s.i.
		3.00 Equivalent % of 10-1			
3.5	1650	3.25	2040	3.2	2120
3.25	1800	5.8	2040	3.5	2250
3.3	1810	2.6	2050	2.6	2260
4.15	1860	7.2	2050	2.8	2270
3.4	1870	3.7	2070	3.3	2290
4.05	1920	3.25	2080	3.4	2330
6.1	1920	3.35	2080		

Average deviation from mean: ±143 p.s.i.

Ultimate elongation: 400 ± 10%

Average tensile strengths from Tables III, IV and V are plotted in Figure 2 against the equivalent percentage of the cross-linking agent. Open circles refer to the high molecular weight rubber treated with 10-1 alone, and the solid circles to the vulcanizates prepared from the low molecular weight rubber. The circles with crosses represent the first set of results given in Table IV; ordinates for these points correspond to the combined percentages of 10-1 and EAD.

It is immediately evident that marked modification of the rubber by incorporation of ethyl azodicarboxylate depresses the tensile strength very little. In fact, if the EAD adduct is considered to be an inert constituent and the tensile strengths are corrected accordingly to the cross-section of the sample devoid of the EAD modified units, the decrease in the corrected tensile strength is only about 200 p.s.i. for 7% modification. The marked diminution in tensile strength for higher proportions of 10-1 (alone) must therefore be attributed directly to the high degree of cross-linking and not to the secondary effect of modification of the structural units such that they are no longer able to fit into the crystal lattice characteristic of the cis-isoprene polymer unit. The ultimate elongation is not affected appreciably by addition of EAD.

TABLE III. Average Tensile Strengths and Elongations for High Molecular Weight Rubber Cross-Linked to Various Extents

Equiv. % of 10-1	No. of test samples	Average ultimate elongation, %[a]	Average T.S., p.s.i.	Mean deviation, ± p.s.i.	Root-mean-square deviation, σ, p.s.i.
0.10	9	1000(±50)	920	204	222
0.20	10	940(±20)	1774	177	194
0.30	17	920(±30)	2288	167	211
0.40	13	850(±20)	2846	184	251
0.50	24	830(±20)	2892	171	209
1.00	33	680(±15)	3102	200	272
1.50	17	570(±25)	2924	200	252
2.00	17	490(±15)	2655	245	288
2.50	11	440(±10)	2353	211	250
3.00	20	400(±10)	2038	143	181
3.20	10	350(±10)	1487	133	171
3.50	14	280(±25)	968	202	242
4.00	16	250(±35)	848	222	265
6.00	13	130(±15)	554	47	59
8.00	13	90(±15)	655	72	79

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[a] Figures in parentheses represent approximate mean deviations of the individual elongation measurements.

Incorporation of EAD in vulcanizates containing less than the optimum proportion (about one equivalent percent) of 10-1 raises the tensile strength significantly. (See the data in the lower portion of Table IV). In the total absence of 10-1, one equivalent percent of EAD yielded a "vulcanizate" exhibiting measurable tensile strength. Films prepared without addition of either 10-1 or EAD were too weak

TABLE IV. Tensile Strengths of Vulcanizates Modified with Ethyl Azodicarboxylate (EAD)

Equiv. % of 10-1	Equiv. % of EAD	No. of test samples	Average ultimate elongation, %[a]	Average T.S., p.s.i.	Mean deviation, ± p.s.i.	Root-mean-square deviation, σ, p.s.i.
1.00	0	33	680(±15)	3102	200	272
1.00	1.0	12	650(±10)	2994	258	284
1.00	2.2	9	655(±10)	2821	172	177
1.00	4.0	15	650(±10)	2755	160	219
1.00	7.0	10	670(±10)	2404	175	215
0.50	0	24	830(±20)	2892	171	209
0 50	0.50	23	805(±20)	2920	287	324
0.30	0	17	915(±30)	2288	167	211
0.30	0.70	28	895(±15)	2605	173	208
0	1.00	10	1275(±70)	450	76	85

TABLE V. Average Tensile Strengths and Elongations for Low Molecular Weight Rubber Cross-Linked to Various Extents

Equiv. % of 10-1	No. of test samples	Average ultimate elongation, %[a]	Average T.S., p.s.i.	Mean deviation, ± p.s.i.	Root-mean-square deviation, σ, p.s.i.
0.30	16	1080(±35)	909	119	135
0.40	16	970(±25)	1505	173	193
0.50	16	890(±15)	1678	185	222
0.70	14	800(±20)	2195	170	207
1.00	33	690(±20)	2376	236	281
1.30	14	630(±15)	2490	148	174
1.50	11	580(±15)	2563	174	248
1.60	20	590(±15)	2550	266	313
1.80	12	530(±10)	2212	144	170
2.00	7	500(±10)	1803	62	74

[a] Figures in parentheses represent approximate mean deviations of the individual elongation measurements.

to be removed from the glass plate on which they were prepared. That the EAD "vulcanizate" was not cross-linked by primary valence bonds in clearly shown by the fact that it dissolved readily in solvents such as benzene and chloroform. Evidently the strongly polar hydrazodicarboxylate substituents on the polymer chains are capable of interacting sufficiently strongly with one another to enhance the effective degree of cross-linking in tensile measurements. Further evidence that these secondary bonds are readily broken in the presence of solvents is found in the observation that incorporation of EAD does not markedly alter the force of retraction of the vulcanizate at 100% elongation, provided that the stretched sample is equilibrated by temporarily swelling with solvent.

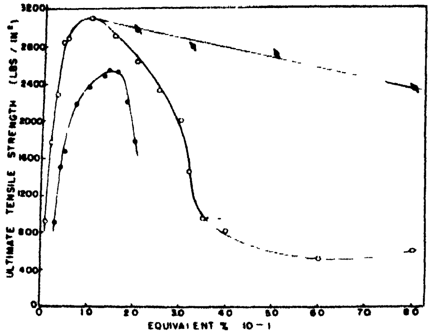

Fig. 2. Tensile strength, in pounds per square inch referred to the initial cross section, plotted against the equivalent percentage (=ρ × 100) of cross-linked units. O, high molecular weight rubber (Table III); ◐, high molecular weight rubber vulcanized with 1.00 equivalent % of 10-1 plus varying amounts of EAD, the ordinate representing the combined percentage of azo compounds; ●, low molecular weight rubber (Table V).

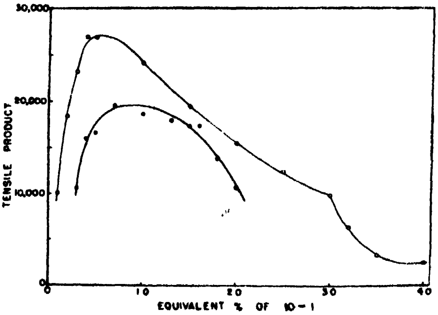

Fig. 3. Tensile strengths referred to the cross section at break for the high (O) and low (●) molecular weight vulcanizates plotted against the degree of cross-linking.

Throughout the tables, and in Figure 2 as well, the tensile strength is referred to the cross section of the sample before deformation. It is sometimes preferred to express the tensile strength in units referring to the cross section of the sample at rupture. The latter tensile strength, or "tensile product" as it has been called, is obtained by multiplying the former tensile strength by the relative length ratio at break. Tensile products for the low and high molecular weight rubbers vulcanized with 10-1 alone are shown in Figure 3 as functions of the degree of cross-linking. The maxima in the tensile product curves occur at lower elongations. A break in the curve for the high molecular weight rubber is indicated at an equivalent percent value of 3.0. Although the reality of this discontinuity is not definitely established, it is possible that it may represent the degree of cross-linking above which crystallization does not occur on stretching under the conditions of our experiments (cf. seq.).

The dependence of the tensile strength of vulcanized rubber on the degree of cross-linking exhibited in Figures 2 and 3 is in qualitative agreement with the results deduced by Gee (3). Significant differences are evident, however, on careful comparison. The maxima in Gee's curves for rubbers cured with sulfur and an accelerator (other than those cured using tetramethylthiuram disulfide)[1] occur at degrees of cross-linking in the range from 1.1 to 1.4 equivalent per cent of cross linked units, which is appreciably beyond the location of the maximum shown in Figure 3 for azo vulcanized rubber of high molecular weight, but only slightly beyond that for the low molecular weight rubber vulcanizates. Our results indicate a broader range over which the tensile product assumes high values, and, in particular, the development of appreciable tensile strength sets in at lower degrees of cross-linking. These differences between our results and those of Gee probably arise from inaccuracies in the statistical theory of rubber elasticity on the basis of which Gee's values for the degree of cross-linking were calculated. Observed forces of retraction for low vulcanizates of known degrees of cross-linking are appreciably greater than the values calculated from theory (2,6). The fact that our maximum tensile strengths are lower than those obtained by Gee and others may not be significant in view of the vast difference in testing procedures and the difference in dimensions of the test pieces.

DISCUSSION

Statistical Analysis Data

Mean deviations given in the next to the last columns of Table III, IV and V are similar in magnitude for all vulcanizates excepting those for which the tensile strength is quite low. In fact, among all vulcanizates for which the tensile strength exceeds 2000 p.s.i. the variations in the mean deviations recorded in Tables III, IV and V are of the magnitude to be expected for sets of 10 to 20 observations (7), assuming that the same probable error of a single observations applies to all sets. Since this assumption appears to be justified, it is permissible to combine the deviations for individual tests on various vulcanizates and thus obtain a set of deviations sufficiently large for statistical analysis.[2] Accordingly, deviations for all individual tests on samples prepared from the high molecular weight rubber using from 0.30 to 3.0 equivalent percent of 10-1 (Table III), and including also the vulcanizates prepared using EAD in addition to 10-1 (Table IV),[3] were combined. The resulting set is comprised of 262 deviations,

[1] Compare the curves shown in Figure 3 of this paper with curves C, D, and E of Figure 5 of reference 3.

[2] The deviations from the means for measurements on 205 different rubber vulcanizates were combined in this manner by O. L. Davies and S. Horrobin, Trans. Inst. Rubber Ind., 12, 85 (1936). In most cases six tests were performed on each sample, but some were represented by fewer tests. With such small numbers of individual tests on each specimen, the combined set of deviations will not be accurately representative of the actual deviations from the true mean values (see above).

[3] Mean deviations for the thirteen tests conducted on a vulcanizate not reported in Tables III and IV were also included in the combined set of 262 deviations. This sample was prepared using 0.8 equivalent % of 10-1 and 0.2 equivalent % of EAD. Tests on the low molecular weight rubber vulcanizates for which the mean tensile strength exceeded about 2000 p.s.i. might also have been included but were not.

each of which represents the difference between the observed tensile strength for an individual test and the average for all tests on the same cure. Owing to statistical errors in the values for these averages, the combined set of deviations may be expected to cover a slightly narrower range than would have been obtained for an equal number of individual tests on the same vulcanizate. The error from this source should be small since the number of tests at each cure was large enough to reduce the probable error of the mean for that cure to a fairly low figure. The mean deviation for the combined set of 262 deviations was 201 p.s.i., the standard deviation was 248 p.s.i. The number of tests for which the deviation falls within each 100 p.s.i. interval is plotted in Figure 4 against the location of the interval (e.g., the number of deviations for the interval -300 to -200 p.s.i. is represented by a point located at -250 along the abscissa). The curve drawn in the figure represents the Gaussian error function for which the standard deviation is that observed for the combined set (i.e., 248 p.s.i.[1] Close agreement between the observed points and the error function is evident.

A somewhat better comparison of the same data with the Gaussian function is afforded by the "probability paper" plot shown in Figure 5. The plot is linear within experimental error throughout most of the range, with some suggestion of small departures at the extremities (see also Figure 4). Thus, there is a slightly greater incidence of very large negative deviations than the Gaussian function would predict, and the incidence of very large positive deviations appears to be too small. However, omission of two or three of the observations in which extreme deviations were observed would eliminate this evidence for asymmetry. On the whole the deviations from the mean are remarkably well represented by the Gaussian function, the apparent skew character at the extremities being indecisive.

In Table VI results of other investigations (8—10) on the distribution of deviations in tensile strength measurements are summarized. In general the distribution is approximately Gaussian, although previous results do not yield as close agreement with the Gaussian function as has been found to be the case for the tests reported here. An excessive number of very low values occurs and a slight deficiency for large positive deviations seems indicated. The presence of the former may readily arise from unobserved flaws in a few of the samples. On the other hand, Braendle and Wiegand (9), using a vulcanizate which presumably contained a small proportion of carbon black, found a markedly skew distribution which cannot be approximated by the Gaussian function.

The view has often been advanced that rupture of the tensile test specimen is initiated invariably at spurious flaws in the test piece,

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[1] In calculating the curve shown in Figure 4, the modulus of precision h in the Gaussian error function:

$$y = (h/\pi^{1/2})\exp(-h^2d^2)$$

where y is the frequency of occurrence of deviations per unit interval at deviation d, has been assigned the value:

$$h = (1/\sigma\sqrt{2})$$

where σ is the observed standard deviation, i.e., 248 p.s.i.

Table VI. Summary of the Results of Statistical Analyses of Tensile Strength Determinations

Investigators	Material and Method	No. of tests	Av. T.S., p.s.i.	Standard deviation, p.s.i.	Distribution of deviations from mean
Braendle and Wiegand (9) (1929)	Samples cut from a commercial inner tube; Scott rubber tester used.	95	2637	170	Skew distribution with excess of low values and deficiency of high ones.
Fric (10) (1928)	Rubber-sulfur (7.5%) vulcanizates tested with Schopper machine.	731	2230	ca. 180	Approximately Gaussian except for frequent occurrence of very low values.
Davies and Horrobin (8) (1936)	205 different vulcanizates, usually six specimens from each, tested with Schopper machine. Individual deviations combined as in present investigation.	ca. 1000		162	Approximately Gaussian except for small excesses of values far from the mean, especially at very large negative deviations.
Present investigation		262	2000 to 3000	248	Close agreement with Gaussian curve, although slight asymmetry is indicated at extremities.

and that the result of a given test merely records the "weakest link" in the series of flaws (of whatever origin) along the length of the specimen. The "true tensile strength", according to this hypothesis, may never actually be realized owing to the intercession of the flaws. The highest observation would therefore represent the closest approach to the "true tensile strength." Proceeding from this concept, it has been common practice to average three measurements which are within 10% of the highest value of the set (11), or to otherwise favor the higher observations.[1]

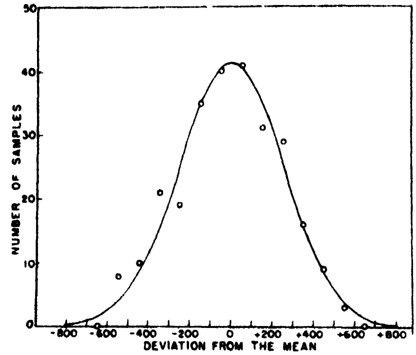

Fig. 4. Distribution of combined deviations from the mean for all tests at 14 different cures. Each point represents the number of deviations falling within a 100 p.s.i. interval.

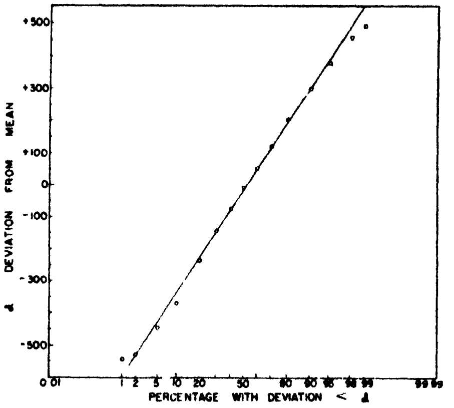

Fig. 5. Probability paper plot of the combined deviations from the mean.

A statistical analysis of the weakest link hypothesis has recently been published by Epstein (12), who shows that a Gaussian (symmetrical) distribution of strength measurements scarcely can be expected on this basis. Furthermore, the average tensile strength should depend on the dimensions of the test piece. Observed results are at variance with these predictions. Not only is the distribution of deviations quite accurately Gaussian under favorable conditions as noted above, but the standard deviations appear to be remarkably uniform for a variety of test conditions including the fifty-fold difference in cross-sectional area of our test pieces as compared with those used in the other investigations. The weakest link hypothesis quite clearly is inapplicable to vulcanized rubber. These facts, in conjunction with the perhaps equally significant approximate constancy of the standard deviation for a wide range in vulcanizate structure (See Tables III and V), should be given foremost consideration in any attempt to formulate an acceptable structural theory of tenacity in such materials.

Entirely apart from theoretical considerations pertaining to the nature of the phenomenon of rupture under stress, the fact that the deviations from the mean assume the Gaussian form invalidates arbitrary selection of the test measurements to be averaged. Rejection of values far from the mean, including very high as well as very low values, may be justified, however.[1] For example, Davies and Horrobin (8) suggested that from a set of five or more observations any which are outside the range $\pm 2\sigma$ may be rejected. Bias resulting from conventional arbitrary selection of the test values has been discussed by Buist and Davies (13).

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[1] The fallacy in these practices has been discussed recently by J. M. Buist and O. L. Davies, India Rubber J., 112, 447-52,454 (1947).

The probable error for a single observation when the Gaussian function is obeyed being 0.675 σ, the probable error applying to the bulk of our measurements (samples of low tensile strength excepted) is 167 p.s.i.. The probable error in the mean of n observations is given by 0.675 $\sigma/n^{1/2}$. Ten or more tests were made for each cure, hence the probable errors in the average tensile strengths given in Tables III, IV and V are about 80 p.s.i., or less. This degree of precision is confirmed by the consistency of the results plotted in Figure 2.

Tensile Strength in Relation to Network Structure

The critical dependence of tensile strength on crystallization of stretched rubberlike materials has often been emphasized. Recently, correlations of tensile strength with the network structure of the vulcanizate have been attempted through consideration of the factors affecting crystallization on stretching (3,6). The relationship of the tensile strength of butyl rubber to the molecular weight before cross-linking (primary molecular weight) has been accounted for semi-quantitatively from this point of view (6). It was shown that the tensile strength at fixed degree of cross linking increases approximately linearly with the fraction of the structure which is permanently oriented by stretching. This fraction, representing the portion of the polymer occurring in chains bounded at both ends by cross-linkages, is given by:

$$w_A = 1 - 2M_C/(M + M_C) \tag{1}$$

where M is the primary molecular weight (the number average should be used), and M_C is the weight per mole of cross-linked units.

$$M_C = 68/\rho$$

where ρ is the fraction of the isoprene units involved in cross-linkages. (100 ρ equals the equivalent percentage of 10-1). Equation 1 may be replaced by:

$$w_A = (\rho\bar{x}_n - 1)/(\rho\bar{x}_n + 1) \tag{2}$$

$$\cong 1 - 2/\rho\bar{x}_n \tag{2'}$$

where $\bar{x}_n$ represents the number average degree of polymerization of the primary molecules.

The investigation on butyl rubber (6) was largely confined to the influence of primary molecular weight on tensile strength, with limited results bearing on the effect of the degree of cross-linking. The bulk of the results were obtained at a fixed degree of cross-linking corresponding to a ρ value of 0.16×10^{-2}. In view of the two chain atoms in the isobutylene unit compared with four for the isoprene unit in rubber, a figure twice this one should perhaps be employed in drawing comparisons with the present results. Even with this alteration, such a comparison would place the principal set of results on butyl rubber in the region well to the left of the maximum in the plot of tensile strength vs. the degree of cross-linking shown for the high molecular weight rubber in Figure 2. Tensile strengths of butyl polymers at about twice this degree of cross-linking (ρ about 0.25×10^{-2}) were lower, however. Thus, it is indicated that the corresponding maximum in the curve for butyl rubber occurs at a very low degree of cross-linking.

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[1] The criterion of Chauvenet for rejection of single observations from a set is of interest in this connection; see A. G. Worthing and J. Geffner, "Treatment of Experimental Data." Wiley, New York 1943, p. 171.

In contrast to the previously reported study of vulcanized butyl rubber, the present results are largely confined to the influence of the degree of cross-linking on tensile strength with only meager results bearing on the role of primary molecular weight. For degrees of cross-linking up to the regions of the maxima, the tensile strength curves shown in Figure 2 for the low and the high molecular weight rubbers are related to one another in the approximate manner to be expected on the assumption that the tensile strength is primarily dependent on the weight fraction w_A of "active" network as given by equations 1 and 2. In order to attain the same tensile strength, the low molecular weight rubber must be cross linked to about three times the extent required for the high molecular weight rubber over this range. Thus, if the primary molecular weight of the latter is assumed to be three times that of the former, roughly the same tensile strength is obtained for the two rubbers when M_c/M, and hence w_A of equations 1 and 2, has the same value for each. The viscosity average molecular weights of the two rubbers (see below) indicated a probable ratio for the primary molecular weights of about five. The difference between the effective molecular weights for the two rubbers may have been narrowed somewhat by the occurrence of chain scission to a small extent during preparation of the vulcanizates. While this possible complication precludes quantitative verification of the direct dependence of the tensile strength on the fraction w_A of the network structure which is permanently oriented by stretching, the results indicate that this factor is of dominant importance throughout the region of low degrees of cross-linking preceding the maximum in the curve. The precipitous rise in the tensile strength with degree of cross-linking in this range provides further conformation for this conclusion, since w_A increases rapidly with ρ for small values of the latter.

The occurrence of a maximum in the tensile strength vs. degree of cross-linking curve and the subsequent decrease in tensile strength for higher extents of vulcanization seem to be related to the diminished ultimate orientation which is attained as the degree of cross linking is increased. It is well known that crystallization sets in at a lower elongation the higher the degree of cross-linking. A recent theoretical treatment (14) of crystallization in stretched rubber indicates that the critical elongation for incipient crystallization (at equilibrium at a given temperature) should vary approximately as the inverse square root of the degree of cross-linking; i.e., directly as the square root of the average length of a chain between cross-linkages. In effect, then, the higher the degree of cross-linking the lower the elongation at which some of the chains become sufficiently oriented to undergo crystallization. Such crystallization increases the effective degree of cross-linking (14) of the chains involved and consequently the degree of crystallinity increases more rapidly with further elongation of the sample. The ultimate degree of crystallinity is rapidly attained, the retractive force rises steeply and rupture occurs at an elongation which may be related, qualitatively at least, to the elongation for incipient crystallization. Therefore, as the degree of cross-linking increases, both the elongation for incipient crystallization and the ultimate elongation decrease in roughly parallel fashion.

The relationship between the orientation of the network structure and the elongation may be approached from consideration of the action of an elongation on the set of "chain displacement" vectors, each of which leads from one cross-linkage to the next along the same chain. On stretching the sample, this set of vectors is distorted from a spherical to an ellipsoidal array. If the sample is stretched to the relative length α, it is readily shown that the fraction of the vectors elongated by the factor κ or greater is given by:

$$f_\kappa = 1 - [(\kappa^2\alpha - 1)/(\alpha^3 - 1)]^{1/2} \qquad (3)$$

which function only gradually approaches until with increase in α for a given value of $\kappa \geqq 1$. It is to be noted that f_κ is independent of the degree of cross-linking. Only those chains which are sufficiently oriented and elongated (the processes of orientation and elongation being mutually related) are potentially capable of participating in the formation of crystallites. The fraction of the chains meeting this requirement clearly will depend sharply on α. Hence, an increase in the degree of cross-linking lowers the elongation at which some of the structure may crystallize, but the fraction which is sufficiently oriented to participate in the formation of crystallites, even at the breaking elongation, is diminished[1]. According to the hypothesis that tensile strength is directly related to the fraction of the structure oriented sufficiently to allow it to participate in the formation of crystallites, the tensile strength should exhibit a corresponding decrease as the degree of cross-linking is increased, in accordance with observation at degrees of cross-linking beyond the maximum in the curve.

The increase in the tensile strength which accompanies rise in testing temperature up to about 100°C. according to certain results (15) cited by Gee (3) also may be explained on the basis of the above considerations. In accordance with the conclusion reached by Gee in this connection, an increase in temperature shifts the onset of crystallization to a higher elongation where a larger fraction of the chains are sufficiently oriented to undergo crystallization. Ultimate elongations were observed (15) to increase with the temperature also.

At higher degrees of cross-linking (i.e., beyond $\rho \times 100 = 3.0$ for the high molecular weight rubber) rupture presumably occurs before the onset of crystallization. In these higher vulcanizates the force of retraction rises rapidly with elongation in accordance with the theory of rubber elasticity (in the absence of crystallization) and may exceed the inherent strength of the material before it is reinforced by crystallization. This idea, mentioned previously by one of the authors (6), has been developed in considerable detail by Gee (3) who suggests it as the major factor responsible for the decline in the tensile strength beyond the optimum degree of cross-linking. In our opinion, however, it assumes importance only under conditions such that the observed tensile strength is very low, e.g., at degrees of cross-linking well beyond the maximum in the tensile strength curve, for very low primary molecular weights, or at temperatures (or dilutions) such that the tensile strength is only a few hundred pounds per square inch. The steep decline occurring near $\rho \times 100 = 3.0$ in the curve shown in Figure 2, and the corresponding intimation of a break in the curve of Figure 3, may be indicative of the degree of cross-linking beyond which crystallization on stretching vanishes.

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[1] The deformation of the residual noncrystalline polymer between incipient crystallization and ultimate rupture of the sample introduces a complication not considered above. The discussion given is intended to be qualitative only.

Effects of Foreign Units on Tensile Strength

The results obtained with the ethyl azodicarboxylate modified vulcanizates (Table IV; also shown in Figure 2) demonstrate that modification of up to 7% of the isoprene units with a substituent which is three times the size of the isoprene unit reduces the tensile strength relatively little. Previous emphasis (3,6) on the influence of small percentages of foreign units on the crystallinity and hence on the tensile strength appears to be unwarranted. Some other explanation is required for the decrease in tensile strength of vulcanizates from butyl rubber having 1.0 or more mole per cent of diolefin as compared with vulcanizates from butyl polymers having half this proportion of the unsaturated unit (6). Likewise, it now appears highly unlikely that the tensile strength of rubber vulcanized with sulfur and an accelerator is materially affected either by cyclization or by non-cross-linking reactions with sulfur, as has been suggested by Gee (3).

According to recent investigations into the nature of crystallization in polymers and copolymers, (16,17) introduction of foreign units at random along the polymer chain will lower the temperature for incipient crystallization, or "melting point", but a large depression requires a correspondingly large proportion of the foreign unit; the effect of the foreign units in the polymer chain resembles that of an impurity on the melting point of a monomeric substance. The degree of crystallinity at a given temperature below the melting point is suppressed to a somewhat greater extent. The most decisive effect of an occasional foreign unit which is incapable of entering the crystal lattice is the limitation of the lengths of the crystallites which may be formed. In the light of these considerations, the observed behavior of the EAD modified vulcanizates suggests that crystallites of great length are unnecessary for the realization of high tensile strength, and, furthermore, that the actual degree of crystallinity is not of direct importance. The crystallites presumably enhance the tensile strength by "cementing" adjacent chains together laterally at various regions along their lengths. Approximately the same tensile strength apparently may be achieved through the participation of each chain of the copolymer (i.e., partially modified polymer) in a number of shorter crystalline regions as through the presence of a fewer number of long crystallites in the unmodified polymer. According to the present results this remains true despite the much smaller degree of crystallinity to be expected in the copolymer. Hence, it is the fraction of the chains of the network structure which are induced to enter into crystallite formation at one or more regions along their lengths which is important, rather than the actual degree of crystallinity. At sufficiently high degrees of modification of the chain units, the tensile strength may fall to a low value owing principally to depression of the melting point to the extent that little or no crystallization occurs on stretching.

The above conclusions are corroborated by the rather small effect of random copolymerization on the tensile strengths of high melting oriented polyamide and polyester fibers (18). Although the tensile strength generally decreases somewhat with increasing proportions of the comonomer, the capacity for exhibition of high tensile strengths by no means destroyed even in 1:1 random copolymers. The residual elongation of the fully drafted fibers is appreciably increased by copolymerization, however.

Over-Cure and Ageing in Rubber Vulcanized with Sulfur and Accelerators

When the curing period is prolonged in the conventional vulcanization of rubber, or if the vulcanizate is heat aged, the tensile strength passes through a maximum beyond which it decreases with further heating. In the light of the above results, this decrease in tensile strength, commonly referred to as "overcure," cannot be attributed to modification of the chain units as suggested by Gee (3). The continued formation of cross-linkages or the occurrence of chain scission (or both) would, however, explain the observed decrease.

The "modulus," or force of retraction, of many compounds similarly passes through a maximum and then declines with further heating. According to the theory of rubber elasticity, the equilibrium force of retraction should be proportional to (19)

$$(1 - 2M/M_c) \cong (1 - 2/\rho \bar{x}_n)$$

The so-called phenomenon of "reversion" of the cure may therefore be due either to rupture of previously formed cross-linkages (a decrease in ρ), or to chain scission which causes M, and $\bar{x}_n$, to decrease. Simultaneous decreases in both tensile strength and "modulus" of highly cross-linked vulcanizates (i.e., beyond the maximum in Figure 2) indicates unambiguously, therefore, that chain scission takes place. Other changes, such as a decrease or increase in the degree of cross-linking, may of course occur simultaneously. It is to be noted that the elastic modulus and the tensile strength are affected differently by variation in $\bar{x}_n$, this being evident from the above expression and the discussion given in the preceding sections. Hence, characterization of the rubber by its force of retraction alone is inadequate.

Gee (3) has shown that two vulcanizates prepared from different compounds but cured for times such that they exhibit the same force of retraction at a given elongation will generally exhibit quite different tensile strengths. The lack of a direct correlation between tensile strength and modulus for rubber specimens vulcanized with different accelerators seems to be general, and it again points to the occurrence of differing degrees of chain scission.

While quantitative results are as yet quite limited, it is now clearly indicated that the apparently irrational dependence of various physical properties of vulcanized rubber on the complexities of the recipe and time of cure can be resolved logically in terms of two extremely simple structure variables: the degree of cross-linking and the primary molecular weight. A third variable, the degree of modification of the chain units, now appears to be of trivial importance, at least insofar as tensile strength is concerned.

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Synopsis

Tensile strengths of natural rubber samples quantitatively cross-linked with decamethylene dis-methyl azodicarboxylate have been determined. The proportion of the azo vulcanizing agent was varied 80-fold, the fraction p of cross-linked units in the products ranging from 0.10×10^{-2} to 8.0×10^{-2}. In spite of the small dimensions of the test specimen (cross section 0.10 in. by about 0.005 in.), the average error for a single observation is similar to that obtained in conventional testing procedures applied to specimens vulcanized with sulfur and

accelerators. Deviations from the mean for 262 tests on 15 different cures are well represented by a Gaussian error function; a slight intimation of skewness is evident only at the extremities of the distribtuion of deviations. These results are incompatible with the commonly held view that rupture of the sample takes place at the "weakest link" in the series of flaws inevitably occurring along the specimen. It would appear that the ability to withstand tensile stress (applied in a specified manner) is an inherent characteristic of the bulk material. The rapid increase in tensile strength with the degree of crosslinking ρ for small values of this quantity is consistent with the conclusion, previously reached in the investigation of the physical properties of butyl rubber (6) that the tensile strength is directly related to the fraction of the structure which is permanently oriented by stretching. At higher degrees of cross-linking (at $\rho \times 100 = 1.0$ to 1.5, depending on the molecular weight of the rubber) the tensile strength passes through a maximum and then declines steadily to quite low values for higher ρ's. This adverse effect of higher degrees of cross-linking is believed to result from the diminished elongation at which crystallization sets in and, hence, the smaller fraction of the network elements sufficiently oriented to participate in crystallite formation. Modification of up to 7% of the isoprene units of the rubber with the monofunctional compound, ethyl azodicarboxylate, depresses the tensile strength of the disazo vulcanized rubber relatively little. Evidently, the limited extent to which these modified (or copolymer) chains may enter into crystallization is adequate to bring about high tensile strength. Lack of direct correlation between modulus and tensile strength for rubbers vulcanized with various sulfur-accelerator combinations can only be explained by assuming that conventional vulcanization processes are accompanied to varying degrees by chain scission reactions. When vulcanized rubber is "over-cured," or heat aged, chain scission becomes excessive.

Résumé

La tension a l'étirement d'échantillons de caoutchouc naturel, quantitativement ponté par le dis-méthyl-azocarboxylate de décaméthylène, a été déterminée. La proportion d'agent vulcanisant a varié du simple à quatre-vingt fois sa valeur, la fraction ρ des unités pontées atteignant de 0.10×10^{-2} à 8.0×10^{-2}. Malgré les faibles dimensions de l'échantillon étudie (section de 0.10 in. sur 0.005 in.), l'erreur moyenne d'une observation determinée est semblable à celle obtenue dans les procédés conventionels appliqués aux échantillons vulcanisés au moyen de soufre et d'accélérateurs. Les déviations de la moyenne pour 262 essais sur 15 preparations différentes sont représentées par une fonction de Gauss; une légère tendance à la déviation est seulement évidente aux extrémités des distributions des déviations. Ces résultats sont incompatibles avec l' ideé généralement admise que l'échantillon se rompt a l'endroit de liaison plus faible, qui se presentent inévitablement sans un échantillon. Il semble que l'aptitude à résister à une force d'étirement soit une propriété caractéristique inhérente au materiel. L'accroissement rapide de la tension d'étirement avec le degré de pontage pour de faibles valeurs de celle-ci

est en accord avec la conclusion, antérieurement formulée dans les recherches sur les propriétes physiques du caoutchouc butylique (6), savoir que la tension d'étirement est directement liée à la fraction de la structure, qui est orientée de façon permanente par étirement. Aux degrés de pontages plus élevés (ρ x 100 = 1.0 jusque 1.5, suivant le poids moléculaire du caoutchouc) la tension d'étirement passe par un maximum, ensuite diminue constamment jusqu'a des valeurs notablement plus basses our des ρ plus élevées. Cet effet inverse des degrés de pontages élevés semble résulter de la diminution de l'élongation, à laquelle la cristallisation débute, et d'une quantité relative plus petite des élements du réseau, orientés suffisamment pour participer à la formation de cristallites. En modifiant les unités isopréniques jusqu'a 7% par un composé monofonctionnel, le azodicarboxylate d'éthyle, on ne provoque qu'une légère diminution de la tension à l'étirement de ces caoutchoucs, vulcanisés par le composé disazoique. Évidemment, la quantité limitée avec laquelle ces chaînes modifiées (ou ces copolymères) peuvent entrer en cristallisation, est favorable à l'obtention de forte tension à l'étirement. Le manque de corrélation directe entre le module et la tension à l'étirement pour des caoutchoucs vulcanisés avec divers mélanges soufre-accélérateur, peut uniquement être expliqué en admettant que les procédés habituels de vulcanisation sont accompagnés à des degrés variables, de réactions de scission de chaîne. Quand le caoutchouc vulcanisé est soumis à une préparation trop longue, ou vieilli à la chaleur, les ruptures de chaînes deviennent trop importantes.

Zusammenfassung

Die Zugfestigkeiten von Naturgummiproben, die quantitativ durch Decamethyl-Azocerboxylat vernetzt wurden, sind festgestellt worden. Das Verhaeltniss des Azo-Vulkanisationsreagenzmittels wurde 80 fach variiert, wobei die Fraktion vernetzter Ketten in den Produkten zwischen 0.10 und 10^{-2} lag. Obgleich der Pruefstab kleine Dimensionen hatte, (Querschnitt 0.10'' x 0.005'') war der Durchschnittsirrtum einer Einzelbeobachtung aehnlich dem, der unter konventionellen Pruefungsmethoden mit Schwefel und Beschleunigern vulkanisierter Proben erhalten wird. Abweichungen vom Durchschnitt fuer 265 Pruefungen und 15 verschiedene Aushaertungen werden durch die Gauss'sche Irrtumsfunktion gut dargestellt nur die Verteilung extremer Abweichungen ist etwas unsymmetrisch. Die Ergebnisse sind unvereinbar mit der haeufig vorkommenden Ansicht, dass der Bruch einer Probe im schwaechsten Gliede einer Serie von Fehlstellen, die unvermeidlicherweise in der Probe vorkommen, stattfindet. Man muesste annehmen, das die Faehigkeit, einem Zuge zu wiederstehen, (wenn er in einer gegebenen Weise angewandt wird) eine Eigenschaft des Stoffes ist. Die schnelle Zunahme an Zugfertigkeit mit dem Grade der Querverbindung fuer kleine Werte dieser Qualitaet ist mit dem Schlusse, der frueher in Untersuchungen physikalischer Eigenschaften von Butylgummi (6) gezogen wurde, vereinbar, dass naemlich die zugfestigkeit direkt von der Fraktion der Struktur abhaengt, die durch Dehnen permanent orientiert wird. Bei hoeheren Vernetzungsgraden (bei ρ x 100 zwischen 1.0 und 1.5 je nach dem Molekulargewicht des Gummis) geht die Zugfestigkeit durch einen Maximalwert

und verringert sich dann ununterbrochen bis zu ganz niedrigen Werten bei höhen ρ's. Dieser nachteilige Einfluss hoher Querverbindungsgrade ist wahrscheinlich eine Folge der verringerten Dehnung, bei der Kristallisation einsetzt, und demgemaess, der kleineren Fraktion der Vernetzen Glieder deren Orientierung gross genug ist, um sie an der Kristallisation teilnehmen zu lassen. Modifizierung bis zu 7% der Isoprenglieder von Gummi mit der monofunktionalen Verbindung Aethyl Azodicerboxylat drueckt die Zugfestigkeit des dis-azo vulkanisierten Gummis nur relativ wenig herab. Offensichtlich genuegt das begrenzte Ausmass, in dem diese modifizierten (oder Mischpolymerisat.) Ketten an der Krystallisation teilnehmen koennen, um höhe Zugfestigkeit sicherzustellen. Der Mangel an Korrelation zwischen Modul und Zugfestigkeit fuer Gummis, die mit verschiedenen Zusammenstellungen von Schwefel und Beschleunigern vulkanisiert wurden, kann nur durch die Annahme, dass konventionelle Vulkanisierungen von verschiedentlich weitgehenden Kettenspaltungsreaktionen begleitet sind, gedeutet werden. Wenn vulkanisierter Gummi "ueberhaertet" wird, oder bei hoher Temperatur gealtert wird, findet eine uebermaessige Kettenspaltung statt.

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Polyelectrolytes. V. Osmotic Pressures of Poly-4-vinyl-N-n-butylpyridonium Bromide in Ethanol at 25° *

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INTRODUCTION

The osmometer has been one of the standard tools of research in physical chemistry for well over a century (1). Theoretical interpretation began with van't Hoff's (2) treatment of Pfeffer's (3) data, which led to the well-known analogy between the behavior of molecules in solution and that of the same number of molecules in the same volume as gas. Deviations from ideal behavior for various real solutions were observed and eventually accounted for in a satisfactory way. Herzog and Spurlin (4) were pioneers in the study of the osmotic pressure of synthetic high polymers: they found that the osmotic pressure of benzyl cellulose solutions in methyl glycol acetate was linear in concentration below 1% of solute by weight, but that the deviations from ideal behavior were very large. Subsequent investigators (5,6) showed that this behavior was a general characteristic of substances of high molecular weight; using a model suggested by Meyer (7), Flory (8) and Huggins (9) independently showed that the deviations from ideality exhibited by polymers were due to entropy terms which arose from the many possible configurations which a chain molecule could assume in solution. We are now able to make reliable measurements of osmotic pressures of polymeric systems and to obtain the molecular weight of the solute from the data. Still more important, the variation of the osmotic coefficients with concentration and temperature can be correlated with the interaction of solute molecules with each other and with those of the solvent.

Electrolytes proved to be one of the major problems in the field of colligative properties of substances of low molecular weight; it was nearly half a century after van't Hoff's work that Debye and Huckel (10) finally succeeded in making a practical calculation of the effect of long range interionic forces on thermodynamic properties of electrolytic solutions. Likewise, in the field of substances of high molecular weights, electrolytic compounds present many unusual properties when contrasted with neutral polymers. One of the classical problems in this field is that of proteins (11), which are, of course, electrolytes of high molecular weight. Lillie (12) found that the osmotic pressure of gelatine solutions depended on the concentration of other electrolytes simultaneously present. Later the importance of the isoelectric point of proteins was understood, and Loeb (13) was able to account for the change of osmotic pressure of protein solutions with electrolyte concentration and pH by means of the Donnan (14) equilibrium. The protein situation is, however, complicated by the fact that the ionogenic groups of the protein, carboxyl and amino, are weak; hence dissociative equilibria must be considered in calculation.

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Compounds of the type we have described in earlier papers (15-17) of this series permit another approach to the problem of thermodynamic properties of polyelectrolytes. Polyvinylpyridine is a typical polymer, much like the familiar polystyrene. By the addition of alkyl halides, it can be converted into a strong polyelectrolyte of known molecular weight and structure. The fact that the resulting electrolyte is strong eliminates the difficulties due to the dissociation processes characteristic of weak acids and bases, including direct hydrolysis or membrane hydrolysis. Synthetic polyelectrolytes offer several other advantages over naturally occurring substances as research material: (a) they are stable; (b) their structure, within reasonable limits, can be varied at will; and (c), nonaqueous solutions can be studied. The significance of the first two points in obvious; the third will be essential in a general treatment of polyelectrolytes, because varying the solvent permits variation of dielectric constant, and it is this variable which controls the intensity of Coulomb forces which are, in last analysis, responsible for the properties which are peculiar to electrolytes. Our knowledge to date of the properties of polyelectrolytes is almost entirely limited to that of proteins, nucleic acids, and polysaccharides in aqueous solution. It is our hope that an investigation of the general field will lead to a better understanding of the special one.

The purpose of this paper is to present the results of a preliminary experimental study of the osmotic pressures of solutions in ethanol of polyvinylbutyl-pyridonium bromides of (number average) degrees of polymerization 730 and 1900. It is not possible yet to treat the general case of Donnan equilibria for strong polyelectrolytes in nonaqueous solvents, because association due to electrostatic interaction reduces free ion concentrations below the corresponding stoichiometric concentrations and because activity coefficients may not be approximated by unity as is frequently (although incorrectly) done in the case of aqueous solutions. We first consider, therefore, the case where polyelectrolyte is the only solute. Here, we have one of the limiting cases of the Donnan equilibrium where no diffusible electrolyte is present (except perhaps for small amounts of impurity) and the observed osmotic pressure is due to the polyions plus the counter-ions which, although small enough to pass through the membrane, are retained on the solution side of the cell by the condition of electrical neutrality. At a given concentration in the dilute range (hundredths of 1% by weight), we find that the osmotic pressure of the polysalt is over an order of magnitude greater than that of the parent polymer. This pressure is, however, very much lower than the limit which would correspond to zero association of counter ions to the polycations, whence we conclude that the polymeric ions carry with them a significant fraction of bromide ions, held solely by Coulomb attraction. By simultaneous measurement of conductance, an estimate of the transference number of the polyion can be made; we find about 0.3 for the sample of low molecular weight and 0.5 for that of high.

By the addition of a large excess of a simple one-one salt (lithium bromide) to the solution, we obtain another limiting case of the Donnan equilibrium where again the observed osmotic pressure is due to the nondiffusible polyelectrolyte. In this case, the association of gegenions to the polyion is markedly increased, as is demonstrated by the resulting sharp decrease in osmotic pressure. By measuring the osmotic pressure of a polyelectrolyte in solutions of a simple electrolyte as solvent, it may be possible to obtain the molecular weight of the polyelectrolyte by extrapolation to infinite ionic strength of added electrolyte (18,19). Further work is in progress.

EXPERIMENTAL

Materials

Polyvinylpyridine. 10 cc. of redistilled (18 mm., 68°) 4-vinylpyridine were diluted with 500 cc. toluene, and 1.0 g. benzoyl peroxide was added. The solution was deoxygenated at room temperature by evacuating until the liquid boiled and then admitting nitrogen; this step was repeated three times. The mixture (under nitrogen) was then placed in a shaking machine in a water bath at 40°. After 21 hours, 13.7 g. polymer (No. 421) was separated by centrifuging; 1.3 g. additional benzoyl peroxide was added, and after deoxygenation, the mixture was put back on the shaker for 8 days. The main lot of polymer (No. 422) was then centrifuged out. The supernatant liquid was completely colorless; presence of oxygen produces a yellow color. The polymer was twice washed with benzene, dried in vacuum, suspended in benzene and stirred for one hour, centrifuged, and finally dried in vacuum at 40° for several days. The total yield was 70.4 grams. Dumas nitrogen was 13.15%, 13.01%; theoretical 13.32%.

Viscosities were measured in ethanol solution; the following values were found; C = 0.408 g./100 cc., $\eta_{sp}/C = 2.04$; 2.13 at 0.532 g./100 cc.; 3.13 at 1.408 g./100 cc. Due to an error in estimation of quantities, the above data are not properly spaced for the conventional extrapolation plot for intrinsic viscosity $[\eta]$. Using the equation (20):

$$\eta_{sp}/C = [\eta] + k' [\eta]^2 C \tag{1}$$

with k' = 0.35, the value we obtained for other polyvinylpyridine (19) samples, we calculate $[\eta] = 1.64$ from the two data at low concentrations.

Polyvinyl-N-butylpyridonium Bromide. One sample of this compound was prepared from the polymer (No. 422) described in the previous paragraph by reaction in nitromethane solution at 55° with *n*-butyl bromide. We designate this as Salt 4115. Bromide was determined by potentiometric titration; found, 31.58%, 31.58%; theoretical, 33.00%. Dumas nitrogens gave 5.50%, 5.54%; theoretical, 5.78%. The bromide is 95.6% of theoretical and the nitrogen is 95.5% of theoretical, so we conclude that each nitrogen carries one ionic bromine. We are indebted to Mr. W. N. Maclay of this laboratory for these analyses.

A solution of Salt 4115 (0.602 g./100 cc. or 0.0237 equivalents bromide per liter) in water of pH 5.84 gave a pH of 3.18, which indicates that some side reaction occurred whereby hydrogen bromide rather than butyl bromide finally added to pyridine nitrogens. Assuming activity equal to concentration, a pH of 3.18 corresponds to a 6.6×10^{-4} normal solution of acid in the 0.0237 normal polysalt solution.

Another sample of salt (No. 612) was also studied. This was prepared from the polyvinylpyridine described in Part II of this series (15), which had a molecular weight of 77,000 (DP 730, about one third that of salt 4112).

Ethanol. Stockroom ethanol was redistilled and the density and specific conductance were measured. The latter varied from 0.043×10^{-6} to 0.073×10^{-6}, which was about 5% of that of the most dilute solution of polyelectrolyte studied.

Lithium Bromide Solution. We used Eimer and Amend C. P. lithium bromide, undried. A sample weighing 245 g. was dissolved in 92.5% ethanol, filtered, and made up to a total of 3109 g. with ethanol. Potentiometric titrations gave an average of 0.7104 moles lithium bromide per kilogram solution. From these data, we calculate that the final solvent was 90.9% ethanol. The density of the solution at 28.0° was 0.856; using the temperature coefficient of ethanol, this gives 0.858 for the density at 25°, whence we find that the solution was 0.610 normal in lithium bromide.

Apparatus

The osmometer used in this investigation was that described by Fuoss and Mead (21); we are indebted to the Research Laboratory of the General Electric Co., for the loan of this apparatus. It was equipped with water jackets (22), through which water, thermostated at 25.00° ±0.03, was circulated.

Membrane corrections were determined in the usual way, with solvent on both sides of the cell. One membrane was used for all the work herewith reported; its correction was 0.18 cm. for ethanol as solvent. With 0.610 N lithium bromide as solvent, the membrane correction was erratic during the first two hours after filling the osmometer; it then became steady at 0.24 cm. This value was reproduced on subsequent fillings. Diffusion of solvent through the membrane was about half as fast with the lithium bromide solutions as with the ethanol soluitions; readings were accordingly taken at 60 second, rather than at 30 second intervals.

In order to check the behavior of the osmometer, we frequently left solutions in the osmometer overnight. As previously pointed out (21). low molecular weight polymer will diffuse into the solvent cell on standing. But the dynamic reading taken the next morning, without changing contents of either half cell, always agreed with the static level which the system had arrived at during standing. Another convenient working check is the difference between levels for rising and falling meniscus, when the rate has reached a definite numerical value. For example, with our membrane and ethanol solutions, when the meniscus was rising at the rate of 0.080 cm./min., the level was always 0.88 cm. below the level at which it would fall at the same rate of 0.080 cm./min. (See Figure 3 of Reference 21.) Finally, we required that two successive fillings of the osmometer give the same dynamic osmotic pressure within 0.05 cm. Apparently, some polymer is adsorbed on the membrane because we found that the osmotic pressure came reproducible after two fillings, if these were allowed to stand in the osmometer at least one hour each. If successive portions of solution and solvent were introduced, measured, and drained in rapid succession, half a dozen or more fillings were necessary before reproducible readings were obtained.

With Polymer 421, the apparent osmotic pressure dropped about 10% on standing at least 5 hours, due to diffusion of material of low molecular weight to the solvent side. Replacement of the liquid in the latter side by fresh solvent always brought the level half-way back to the initial value, in accordance with our earlier observations. We attempted to determine the actual weight of the diffusible material. In one experiment, a solution (1.44 g./100 cc.) gave an initial osmotic pressure of 6.56 cm., which dropped to 6.04 cm. on standing overnight, a decrease of nearly 10%. The contents (20 cc.) of the solvent half-cell were then drained into previously weighed weighing bottle and the liquid was carefully evaporated. No detectable residue was found; i.e., certainly less than 0.5 mg. were responsible for the 0.52 cm. drop in osmotic pressure. The solution half-cell contains 20 cc., of which half is in contact with the membrane; hence about 0.144 g. whole polymer were originally present in the solution half-cell adjacent to the membrane. To give a 10% decrease in osmotic pressure, the less than 0.5 mg. (0.3% of whole polymer) could not possibly have had a molecular weight greater than 3000. Actually, the value was probably much lower than this, because 0.5 mg. is a very liberal estimate of weighing error; had we taken 0.1 mg., for example, the upper limit would have been only 600. The impurity might have been benzoic acid from the catalyst. In any case, this observation suggests that osmotic pressures obtained after dialysis of the sample are more representative of the polymer than are those obtained by the dynamic method shortly after filling the osmometer.

The most convenient units for practical laboratory work are pressures π in centimeters of solvent and concentrations w in grams of solute per kilogram solution. In these units, the limit of (π/w) at zero concentration is $1033\,RT/M = 25{,}280/M$, where M is the number average molecular weight. In conventional units (p in g./cm.^{2}, and C in g./100 cc.), the ratio p/C is simply $10\,\pi/w$ because the density appears in both numerator and denominator on converting units ($w = 10\,C/\rho$; $\pi = p/\rho$).

RESULTS

The osmotic pressures of Polymer 421 are given in Table I. The second column gives π_0, the initial dynamic value of the osmotic pressure, and includes the contribution due to diffusible impurity. On standing, the osmotic pressure drops to $(\pi_0 - \delta\pi)$; on refilling the solvent half-cell with fresh solvent, the dynamic pressure measured immediately rises to $(\pi_0 - \delta\pi/2)$. On standing, the pressure again drops to (π_0 - $\delta\pi$) as half of the remaining material of low molecular weight diffuses out of the solution half cell. Repetition of this process gives a final dynamic and static osmotic pressure π_∞ = (π_0 - $\delta\pi$). The values of π_∞ are given in the third column of Table I; it will be noted that (π_0 - π_∞) is proportional to w, as should be the case if the drop is due to a fixed percentage of diffusible impurity.

TABLE I. Osmotic Pressures of Polymer 421 in Ethanol at 25°

w	π_0	π_∞	C	p_0/C	p_∞/C
3.03	0.54	0.48	0.243	1.78	1.58
5.64	1.27	1.12	0.452	2.25	1.99
8.07	1.94	1.76	0.648	2.40	2.18
9.43	2.49	2.27	0.756	2.64	2.41
17.94	6.35	5.86	1.440	3.54	3.27

The data are linear on the conventional plot of pressure over concentration versus concentration; the open circles of Figure 1 correspond to p_0/C and the solid ones to p_∞/C. The former extrapolated to M = 165,000 and the latter to M = 195,000. As explained in the previous section, we believe the latter figure to be more accurately descriptive of the polymer. Polymer 422 was not significantly different from No. 421. Two solutions with C = 0.953 and 0.556 g./100 cc. gave p_∞/C = 2.72 and 2.35, respectively; these values are to be compared with 2.65 and 2.08, the values interpolated from Figure 1 for No. 421 at the same concentrations. The density of a pressed disk of polyvinylpyridine was found to be 1.153 g./cc. Using this value, and the slope 1.43 of the p/C - C plot, we find μ = 0.464.

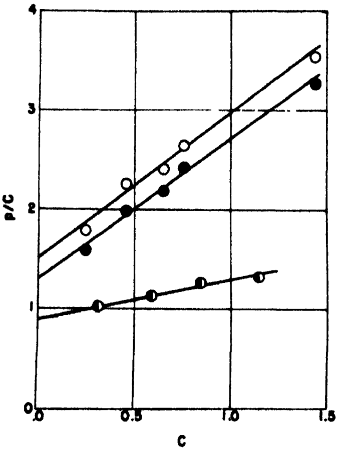

Fig. 1. Osmotic Pressures. Open circles, initial values for Polymer 421; solid circles, final values; half-black circles, Salt 4115 in 0.610 normal alcoholic lithium bromide solution.

As might be expected, the polyelectrolytes gave a much higher osmotic pressure at a given weight concentration than the corresponding parent polymers, due to the effect of the counter ions. For example, the average degree of polymerization of Salt 4115 is approximately 1900; if no association occurred, the number of particles from a given weight of the salt would be 1901 times those from the same weight of polymer; 1900 bromide ions and one polycation. Actually, the pressures were only between 10 and 100 times as large as that of the polymer, indicating a rather high degree of association of counter ions to polycations.

The behavior on standing in the osmometer of the polyelectrolytic solutions was markedly different from that of solutions of electrically neutral polymers. On standing overnight, the apparent osmotic pressure dropped from 20 to 35% of the dynamic value obtained at "zero" time (as soon as temperature equilibrium was established after filling). But on refilling the solvent half-cell with fresh solvent, the pressure rose much more than half the drop. Our tentative explanation is that hydrogen bromide was responsible. (We recall that the salt gave a slightly acid solution in water.) Pyridine is a very weak base and in solution, most of the hydrogen bromide would be free to diffuse through the membrane. We have here a case of Donnan equilibrium where a small amount of diffusible electrolyte is present with a large excess of nondiffusible electrolyte, and where practically all of the diffusible electrolyte is driven through the membrane, where it then exerts a large counter pressure. On refilling the solvent half-cell, the osmotic pressure rises nearly to that corresponding to the polysalt alone. The magnitude of this effect is shown in Table II where π_0 and π_∞ have the same significance as before, while π' is the dynamic (and static) value found for the initial filling of the cell after it had remained in the cell for at least 6 hours but before refilling the solvent half-side of the cell. It will be noted that ($\pi_0 - \pi'$) is linear in w, corresponding to a constant percentage of diffusible electrolytic impurity. The values of ($\pi_0 - \pi_\infty$) for the polysalt are much smaller than for the parent polymer; presumably, most of the impurity of low molecular weight in the latter was extracted during the preparation of the salt from the polymer.

TABLE II. Variation of Osmotic Pressure Due to Dialysis

w	π_0	π'	π_∞	π_∞/π_0
		Salt 4115		
0.195	0.58	0.37	0.51	0.880
0.242	0.70	0.48	0.63	0.900
0.334	1.03	0.72	0.91	0.884
0.863	2.46	1.96	2.34	0.952
1.309	3.66	2.93	3.61	0.986
1.779	4.65	3.81	4.43	0.953
2.460	6.60	5.29	6.48	0.982
		Salt 612		
0.177	0.70	0.48	0.64	0.915
0.322	1.34	1.02	1.21	0.904
0.582	2.49	2.02	2.32	0.932
0.863	3.48	2.86	3.19	0.916
1.583	6.18	5.12	5.77	0.934

The membrane correction of 0.18 cm. has been applied to all the data of Table II. As will be shown later in the discussion, there is some doubt concerning the proper value of membrane correction to be used in the presence of ions; there are indications that it varies with electrolyte concentration, and further study is needed.

TABLE III. Conductances of Polyelectrolytes in Ethanol at 25°

10^3c	Λ	10^3c	Λ
	Salt 4115		
Series 1		Series 3	
0.3108	3.93_8	0.621	3.75_1
0.7416	3.69_6	0.769	3.75_8
3.604	3.31_3	1.062	3.66_8
13.093	2.89_2	1.721	3.55_3
Series 2		2.745	3.46_2
16.14[a]	2.766	4.165	3.32_8
68.96	1.997	5.660	3.24_7
258.4[b]	1.433	7.827	3.12_4
	Salt 612		
0.563	3.70_3	2.751	3.12_4
1.027	3.43_3	5.046	2.92_9
1.854	3.25_7		

[a] $\eta/\eta_0 = 1.65$

[b] $\eta/\eta_0 = 9.55$; $\rho = 0.833$

Conductances were also determined using the same apparatus and technique as before (16). In discussion of conductance data, weight concentrations (C or w) are meaningless, and it is therefore necessary to refer the data to concentrations c, expressed as stoichiometric equivalents of bromide ion per liter. The relation between the three concentration scales is given by:

$$c = 10C/m = \rho w/m \tag{2}$$

where ρ is density and m is the equivalent weight of a monomer unit. In Table III, we give the equivalent conductances Λ of the salts, which were calculated from the observed total[1] specific conductances κ by the usual definition:

$$\Lambda = 1000\,\kappa/c \tag{3}$$

In Series 1, the density of the alcohol was 0.8041, corresponding to 93.5% ethanol, and the solvent conductance was 0.067×10^{-6}. The corresponding figures for Series 2 and 3 and for Salt 612 are: 0.8052, 93.1%, 0.073×10^{-6}, 0.8072, 92.4%, 0.043×10^{-6}; and 0.8066, 92.6%, 0.048×10^{-6}. Different lots of alcohol had slightly different ethanol contents, and hence different viscosities and dielectric constants;

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[1] For discussion of solvent correction, see page 253 of reference (15).

effects of these variations are not pertinent to the present discussion. Approximate viscosities of two of the most concentrated solutions were measured; it will be noted that the relative viscosity increases very rapidly with concentration, reaching nearly 10 in a 6.5% solution.

In order to determine the effect of the presence of excess simple electrolyte on the properties of the polymeric electrolyte, both osmotic pressures and conductances of Salt 4115 were measured in 0.610 normal lithium bromide solution as solvent. The data are summarized in Table IV. It was noted that the osmotic pressures were always somewhat erratic for an hour or so after replacing solvent in the solution half-cell with solution, but steady reproducible values were obtained after about two hours. The π_0 figures of Table IV therefore refer to data taken after this time. On standing overnight, the osmotic pressure remained constant or else increased somewhat. This observation supports our guess that the large decrease and subsequent large regain for the polyelectrolyte alone (Table II) were mostly due to hydrogen bromide, because the small amount of this impurity would be invisible in the presence of the large excess of lithium bromide. It will be noted that the p/C values (averaged over π_0 and π_∞) are of the same order of magnitude as those of the neutral polymer. In the fifth column of Table IV are given the specific conductances of the solutions and in the last, the decrease in specific conductance produced by the addition of polyelectrolyte to the lithium bromide solution.

TABLE IV. Properties of Salt 4115 in 0.610 N Alcoholic Lithium Bromide Solution

C	π_0	π_∞	p/C	$10^3\kappa$	$-10^3\Delta\kappa$
0.000	-	-	(0.90)	7.563	0.000
0.312	0.34	0.41	1.02	7.541	0.022
0.586	0.77	0.77	1.13	7.510	0.053
0.846	1.22	1.27	1.26	7.448	0.115
1.147	1.75	1.75	1.31	7.447	0.116

From the specific conductance of the lithium bromide solution used as solvent, we calculate $\Lambda = 12.40$ for lithium bromide at 0.610 normal in ethanol. By Walden's rule we estimate Λ_0 for this salt to be 82.5; hence there is also considerable ion association of the univalent ions in this solvent.

DISCUSSION

It is first necessary to comment on the membrane correction for the data on the polyelectrolytes. We found 0.18 cm. with ethanol on both sides of the membrane, and 0.24 cm. with 0.610 N lithium bromide solution on both sides. In Figure 2, we have plotted the p/C data for both polymeric salts; the upper curve for each salt gives the data based on π_0 values (cf. Table II) without membrane correction and the lower curve gives the p/C values based on π_0, using a membrane correction of 0.18 cm. As might be expected, there is no significant difference at higher concentrations. But in the range of low concentrations, the corrected curve for Salt 4115 is considerably flattened, and for Salt 612, a maximum around 50 mg./100 cc. appears. The latter certainly is fictitious because the limit at zero concentration for p/C must be approximately[1] 1000 and the curve must necessarily be concave-upward. It thus appears that 0.18 cm. is an over-correction for membrane assymetry and we shall disregard the correction for the present.

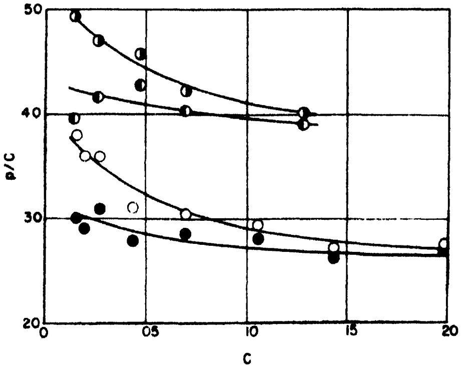

Fig. 2. Osmotic pressures of polyelectrolytes. Right-black circles, Salt 612, uncorrected initial values; left-black circles, Salt 612, corrected initial values. Open circles, Salt 4115, uncorrected initial values; solid circles, Salt 4115, corrected initial values.

One other source of error must be mentioned: the small increment $\Delta\pi$ of osmotic pressure ($\pi_0 - \pi_\infty$) which we tentatively ascribe to residual impurities. Again, this error becomes negligible at higher concentrations, but affects the shape of the curve at low concentrations. As seen in Table II, $\Delta\pi$ is approximately constant, and its effect is obviously one which increases with decreasing concentration on a p/C plot. Since the conductance data necessarily include contributions from electrolytic impurities, we shall use the π_0 values for comparisons between these two sets of data.

Regardless of these two uncertainties, three significant differences between the p/C curves for the polyelectrolytes and those of the parent polymers are obvious, on comparing Figures 1 and 2. First, the magnitude of the osmotic pressure of the polyelectrolytes is by far greater; for example, at 0.2 g./100 cc. (the highest concentration measured for the polysalt and the lowest for the polymer), the p/C values are, respectively, 28 and 1.8. Second, the osmotic pressure-concentration ratio of the polysalt increases with dilution while that of the polymer decreases. Third, the p/C - C plots are linear for the polymer and curved for the polyelectrolyte. These characteristics are, of course, to be expected for a salt of the type under consideration. The osmotic pressure is high, because each free bromide ion which is not bound to (or in) a polycation by Coulomb forces contributes just as much to osmotic pressure as a single macromolecule. As dilution increases, more and more bromide ions escape from the electrostatic fields of the large positive ions, and the osmotic pressure increases correspondingly. Finally, since electrostatic forces are involved, linearity in the first power of concentration is not to be expected, because neither concentrations of free ions nor activity coefficients are linear in concentration.

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[1] In the hypothetical limit of zero concentration, no bromide ions would be associated with the polycation; hence a polysalt with degree of polymerization n would give (n + 1) particles, and the limiting osmotic ratio would be $(p/C)_0 = 2.53 \times 10^5/(1/m + 1/M) \approx 2.53 \times 10^5/m$, where m is the molecular weight of the monomer unit. Since m = 242.2, and the compound analyzed to 95.2% theoretical bromide, the effective monomer weight is then 242.2/0.952 = 254. Practically, this limit cannot be reached because at any low but finite concentration, the positive field of the polycation is enormous, and a certain number of anions will be associated with the cations. In other words, the solution will act as if to each molecule of polyelectrolyte, there corresponded (n - m + 1) particles, where m changes only extremely slowly with concentration. A similar paradox has been discussed for the case of conductance; cf. p. 257 of Ref. (15).

Dissociation of the polyelectrolyte in alcohol is far from complete, as in evident from the disparity between 1000, the theoretical limit of p/C and the observed values of 30-50. Even at this range of dielectric constant, however, it is interesting to note that the salt of lower molecular weight gives the higher osmotic pressure (cf. Figure 2) at a given weight concentration. It should be emphasized that this is not due to the same cause which operates in the case of neutral materials, where a given weight contains more (whole) molecules of material of lower molecular weight. Rather, the higher osmotic pressure of the polyelectrolyte of lower molecular weight is due to the greater number of bromide ions free at a given concentration due to its relatively weaker electrostatic field. In other words, the Coulombic binding capacity for bromide ions is greater if a given weight of polycation is present as fewer, but larger more highly charged units.

When an excess of simple one-one electrolyte is added to the polysalt, we would expect a marked decrease in osmotic pressure because the excess of counter ions would in the limit completely suppress the dissociation of the polyvalent electrolyte. As shown in the lower curve of Figure 1, this is precisely what happens when 0.610 normal lithium bromide solution is used as the solvent for Salt 4115. The osmotic pressure is depressed below that of the parent polymer and the curve is now linear, extrapolating to an intercept of 0.90, with a much smaller slope (larger μ value) than that of the neutral polymer in ethanol. If, on the average, one free bromide ion were present for each molecule of polyelectrolyte, the p/C intercept for the polysalt in lithium bromide solution would be a little lower than 1.30, that for the parent polymer; $1.30 \times (105)/(242/2) = 1.13$. If suppression were complete, the intercepts for Polymer 421 and Salt 4115 should be in the inverse ratio of the weights of the monomer units, $242/105 = 2.30$, which would correspond to an intercept of 0.57 for the salt. Actually, they are in the ratio $1.30/0.90 = 1.45$, indicating that on the average less than one free bromide ion is present per molecule of polyelectrolyte. It will be interesting to study the osmotic pressures of polyelectrolytes in different concentrations of added salt, to see if an extrapolation to "infinite concentration" of added electrolyte will give the molecular weight of the polyelectrolyte, in analogy to our result for viscosity (18). We also plan to study the dependence of the slope on concentration and type of added electrolyte.

The conductance curves for the two salts (612 and 4115) are shown in Figure 3. For comparison, our previous data (15) for another sample of electrolyte (Salt II) prepared from the same parent polymer as Salt 612 are also shown. The curve for Salt 612 is lower by about 10% and not quite parallel to the previous curve; we can offer no explanation for this discrepancy. More experience in preparation and purification of salts is obviously needed. One significant difference between Salts 612 and 4115 appears: in our working range of concentrations, Salt 4115 shows a marked curvature on a log Λ - log c plot, while the data for Salt II give a linear plot. The log Λ - log c plot must eventually become concave to the concentration axis for all salts; the range of concentration where this will occur will depend on molecular weight. Until more data are available on a wider variety of systems (especially with fractionated materials), it seems pointless to speculate further.

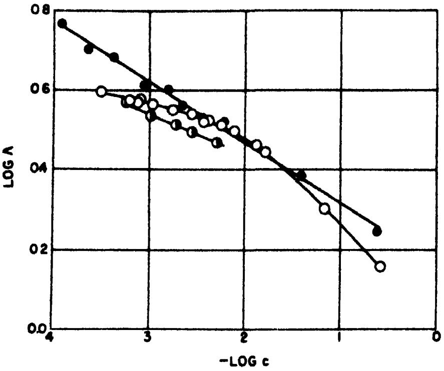

Fig. 3. Conductance curves. Solid circles, data of Reference (15); open circles, Salt 4115; half-black circles, Salt 612.

The behavior at the higher concentrations gives some information regarding local hydrodynamics in these solutions. The macroscopic viscosity of the most concentrated solution was nearly ten times that of the solvent, while that at one sixteenth the concentration was less than double. (Cf. Table III.) Still, no corresponding sharp drop in conductance occurs in this range of concentration. We can only interpret this to mean that the ions find a different (lower) resistance to their motion from that which we measure with a capillary viscometer. The situation recalls the old observation (23) that the conductance of potassium chloride in gelatin solution does not undergo a sharp change when the solution sets to a gel.

If we neglect the electrostatic effects of interionic forces, we may obtain an upper estimate for the "degree of dissociation" of the polyelectrolyte by classical methods. If the electrolyte were completely dissociated, we would have $\pi/w = 25273/m \approx 100$ and on our assumption then, the value of π/w is approximately equal to 100γ, the degree of dissociation. Using Walden's rule, we estimate the equivalent conductance Λ' of the bromide ion in our ethanol to be 53. The product $\gamma\Lambda'$ then gives the contribution of the bromide ion to the total conductance, and we are thus able to estimate the transference number of the bromide ions in the polyelectrolyte. Subtracting this quantity from unity, we obtain a value for the transference number

N+ of the polycation. The results of this calculation are given in Table V. The agreement with the γ values calculated on the basis of an entirely different set of assumptions (15) (except the neglect of interionic forces) is surprisingly good. This consistency must, of course, be due to compensation of errors because the neglected interionic terms are quite large at a dielectric constant of 30, even at ion concentrations of the order of 2 x 10^{-4}, the highest estimated in Table V. Comparing relative values, however, it is interesting to note that the calculated transference number is higher for the polysalt of higher degree of polymerization; since friction coefficient increases less rapidly than DP, we would expect mobility to be higher for the same degree of dissociation for the polyion of higher molecular weight.

TABLE V. Transference Numbers of Polycations

10^3c	$\pi_{\alpha}/100w$	$\gamma\Lambda'$	N^+
		Salt 612	
0.563	0.049	2.60	0.30
1.027	0.047	2.49	0.27
1.854	0.046	2.44	0.25
2.751	0.042	2.22	0.29
5.046	0.040	2.12	0.27
		Salt 4115	
0.621	0.038	2.02	0.46
0.769	0.036	1.91	0.49
1.062	0.036	1.91	0.48
1.721	0.031	1.64	0.54
2.745	0.030_5	1.62	0.53
4.165	0.029	1.54	0.54
5.660	0.027	1.43	0.56
7.827	0.027_5	1 46	0.53

The addition of polyelectrolyte to lithium bromide solutions results in a decrease of conductance, as shown in Table IV. This result can be accounted for on the basis of the observed osmotic pressures in the mixed electrolytes. There we found less than an average of one free bromine ion per polyion; due to the high concentration of charge in the polyion, it could hold more than a stoichiometric equivalent of bromide ions and the unpaired lithium ions would then contribute to osmotic pressure. This extra immobilization of bromide ions would then result in a decrease of conductance. A similiar result has been observed in the case of gelation: Rettig (24) found that the conductance of gelation-salt mixtures was less than the conductance of the salt solution when salt was in excess.

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Synopsis

The osmotic pressures of two samples of poly-4-vinyl-N-n-butylpyridonium bromide (average D. P. 730 and 1900) were measured in 93% ethanol in the concentration range 0.02-0.20 g./100 cc. The osmotic pressures were higher than those of the corresponding parent polymers, due to partial dissociation of bromide ions. Because of the low dielectric constant ($\epsilon' = 28$) of the solvent and the high concentration of positive charge in the polycations, however, a large fraction of the bromide ions ($\geqslant 95\%$) were bound by electrostatic attraction to the cations and contributed neither to osmotic pressure nor to conductance. Unlike neutral polymers, the ratio (osmotic pressure over concentration) increases with dilution, due to increasing dissociation with dilution. Addition of an excess of a simple one-one electrolyte (lithium bromide) almost completely suppressed the dissociation of the polysalt and gave osmotic pressures of the same order of magnitude as those of the neutral polymers. The resulting curves were linear, with a considerably smaller slope than for the parent polymer. Combining the results on osmotic pressure with conductance data, the transference numbers of the polycations were estimated to be 0.28 and 0.52 for degrees of polymerization 730 and 1900 respectively. The conductance of lithium bromide is decreased by the addition of these polyelectrolytes, possible due to the association of an excess of anions to the polycations under the influence of their electrostatic fields.

Résumé

Les pressions osmotiques de deux échantillons de bromure de poly-4-vinyl-N-n-butylpyridonium (D.P. moyen: 730 et 1900) ont été mesurées en solution dans l'alcool éthylique 93% à ces concentrations variant de 0.02 à 0.2 gr. dans 100 cc. Les pressions osmotiques sont plus élevées que celles des polymères correspondants, dont ils dérivent, à cause de la dissociation partielle des ions bromures. À cause de la faible constante diélectrique du solvant ($\epsilon' = 28$), et à cause de l'accumulation de charges positives dans les polycations, une grande partie des ions bromures ($\geqslant 95\%$) restent toutefois attachés par attraction électrostatique aux cations, et ne contribuent donc ni à la pression osmotique ni à la conductivité. Contrairement aux polymères neutres, le rapport (pression osmotique/concentration) s'accroît avec la dilution, par suite d'une dissociation progressive par dilution. Par addition d'un excès d'un électrolyte simple univalent (bromure de lithium) on peut supprimer pratiquement de façon complète cette dissociation du polyélectrolyte, et la pression osmotique l'on obtient, est du même ordre de grandeur que celle du polymère neutre. Les courbes résultantes sont linéaires; la tangente à cette droite est notablement plus faible que celle pour le polymère, dont le polyélectrolyte dérive. En combinant les résultats de pression osmotique avec ceux de la conductivité, on trouve des nombres de transport pour les polycations, égaux à 0.28 et 0.52 pour les degrés de polymérisation 730 et 1900 respectivement. La conductivité du bromure de lithium est diminuée par addition de ces polyélectrolytes, peut-être par suite d'une association d'un excès d'anions ver les polycations, sous l'influence du leurs champs électrostatiques.

Zusammenfassung

Die osmotischen Drucke von zwei Proben von Poly-4-Vinyl-N-n-Butylpyridoniumbromid (durchschnittlicher Polymerisationsgrad 730 und 1900) wurden in 93%igem Ethylalkohol in dem Konzentrationsbereich 0.02-0.20 g./100 cm.^{3} gemessen. Die osmotischen Drucke waren hoeher als die der entsprechenden Ausgangspolymerisate wegen teilweiser Dissoziation der Bromid-Ionen. Wegen der niedrigen dielektrischen Konstante ($\epsilon' = 28$) des Loesemittels und der höhen Konzentration der positiven Ladung in den Polykationen, war ein Grossteil der Bromid-Ionen ($\geqslant 95\%$) durch elektrische Anziehungskraefte an die Kationen gebunden und trug infolgedessen weder zum osmotischen Druck noch zur Leitfaehigkeit bei. Im Gegensatz zu neutralen Polymerisaten steigt das Verhaeltnis des osmotischen

Druckes sur Konzentration mit Verduennung, wegen der steigenden Dissoziation, an. Zugabe eines Ueberschusses einfacher ein-einwertiger Elektrolyte (Lithium-Bromid) unterdrueckte fast gaenzlich die Dissoziation des polymerischen Salzes und ergab osmotische Drucke derselben Groessenordnung wie die neutralen Polymerisate. Die auf diese Weise erhaltenen Kurven waren linear und betraechtlich flacher als die des Ausgangspolymerisates. Auf Grund der osmotischen Druck- und Leitfaehigkeitsdaten wurden die Uebertragungszahlen der Polykationen auf 0.28 und 0.52 geschaetzt, fuer Polymerisationsgrade von 730 und 1900. Die Leitfaehigkeit von Lithium-Bromid wird durch Zugabe dieser Polyelektrolyte verringert, moeglicherweise wegen der Assoziation des Ueberschusses von Anionen unter dem Einfluss des elektrostatischen Feldes der Polykationen.

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Compléments à l'Étude de la Statistique des Chaînes Moléculaires en Solution Diluée

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INTRODUCTION

Considérons une chaîne moléculaire qui, pour la simplicité de l'exposé, sera constituée par suite d'atomes de carbone liés entre eux par des liaisons simples (1).

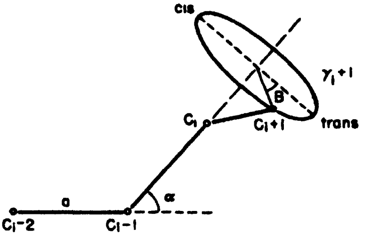

Figure 1

Nous avons représenté sur la figure 1 les positions des centres de quatre atomes successifs de la chaîne: si les points C_{i-1}, C_i, C_{i+1} sont choisis dans le plan de la figure, le point C_{i+1} peut prendre, par suite de l'agitation thermique des positions différentes situées sur le cercle Γ_{i+1}, base du cône dont le demiangle au sommet α est égal au supplément de l'angle de valence. Dans le cas d'une chaîne aliphatique $\alpha = 70°29$, $\cos \alpha = \mu = 1/3$ et l'intervalle entre deux atomes successifs C_i et C_{i+1}, appelé longueur du chaînon, est constant et égal à:

$$a = 1.54 \text{ A}.$$

Nous repérons les positions de C_{i+2} sur le cercle par les valeurs correspondantes de l'angle B que font entre eux les plans de la figure et le plan defini par C_{i-1}, C_{i+1}, C_{i+1}.

Par suite de l'agitation thermique une chaîne moléculaire comprenant N chaînons prend des configurations diverses et l'un des problemes fondamentaux est de déterminer l'écart quadratique moyen δ^2 entre les extrémités C_0 et C_N de la chaîne.

Il est clair que la valeur de δ^2 dépend de a, de α et de la loi de répartition statistique de chaque centre tel que C_{i+1} sur le cercle de base du cône de valence.

Le cas le plus simple est celui où toutes les positions sont possibles et également probables, c.à.d. celui des rotations dites "libres." Il a été examiné par Guth et Mark (2) et par W. Kuhn (3), qui ont établi à partir d'un résultat de Eyring (4) que:

$$\delta^2 = Na^2 \frac{1+\mu}{1-\mu} \qquad (1)$$

où $\mu = \cos \alpha$ dans le cas où N est très grand devant l'unité.

Dans le cas général l'expression complète donnée par Eyring (4) et aussi par Delange (5) est la suivante:

$$\delta^2 = a^2 \frac{N(1 - \mu^2) - 2\mu + 2\mu^{N+1}}{(1 - \mu)^2} \qquad (2)$$

Dans les cas des chaînes carbonées où $\mu = 1/3$ les valeurs de δ^2 calculées par l'expression 1 donnent un résultat qui diffère par excès de moins de 10% de la valeur calculée par l'expression 2 quand N devient supérieur à 10. L'équation 1 représente donc ainsi, dans le cas des rotations libres, une approximation largement suffisante.

Mais l'étude des vapeurs d'hydrocarbures de faible masse moléculaire montre qu'en général toutes les positions de l'atome de carbone sur le cercle de base du cône de valence ne sont pas également probables et il doit en être de même dans le cas des solutions.

En général à chaque valeur de B correspondra une énergie interne W différent. Si, par exemple, on suppose que dans la solution, la position "trans" correspond à un minimum de W, cette position sera favorisée parmi toutes les autres et il s'en suivra que l'écart δ^2 sera plus grand que dans le cas des rotations libres.

Nous nous proposons de donner ci dessous une brève analyse des résultats obtenus.

Nous remarquerons d'abord que, dans le cas des rotations libres les valeurs moyennes:

$$\eta = \cos B$$

$$\varepsilon = \sin B$$

pour toutes les positions de C_{i+1} sont nécessairement nulles. Il n'en est plus de même dans les cas ou les rotations ne sont plus libres. Si la distribution des positions de chaque point C_{i+1} sur la base du cône est symétrique par rapport au plan C_{i-1}, C_i, C_{i+1} le coefficient ϵ est nul et δ^2 dependra uniquement de a de μ et de η ; c'est le cas que nous envisagerons.

Le calcul de l'écart quadratique moyen entre les extrémités de la chaîne se divise ainsi en deux parties.

1. Exprimer la valeur de δ^2 correspondant à une valeur donnée de η .
2. Exprimer la valeur de η correspondant à une distribution de l'énergie interne W(B).

CALCUL DE δ^2 EN FONCTION DE η .

Quand η est assez petit pour que η^2 soit négligeable devant l'unité (chaîne à rotation presque libres) l'un de nous (6) avait déjà montré que l'on a:

$$\delta^2 = Na^2 \frac{1 + \mu}{1 - \mu} (1 + 2\eta) \qquad (3)$$

η étant positif ou négatif selon que la position trans ou cis est favorisée. Dans le même travail le cas opposé avait été examiné; c'est celui où la chaîne présente des configurations très voisines de la configuration tendue au maximum, c.à.d. du zig-zag planaire de longueur $L = Na \cos\frac{\alpha}{2}$ et l'on avait montré alors que:

$$\delta = L \left\{1 - \frac{2N}{3} \sin^2\frac{\alpha}{2}(1 - \eta)\right\} \qquad (4)$$

Un peu plus tard Benoît (7), s'appuyant sur un travail inédit de P. Debye résolut le problème dans sa généralité et montra que, pour une valeur quelconque de η comprise entre -1 et +1 on avait:

$$\delta^2 = a^2\left\{\frac{\mu-\lambda_2}{\lambda_1-\lambda_2}S_1 - \frac{\mu-\lambda_1}{\lambda_1-\lambda_2}S_2\right\} \tag{5}$$

où S_1 et S_2 sont les valeurs prises par S:

$$S = \frac{N(1-\lambda^2) - 2\lambda + 2\lambda^{N+1}}{(1-\lambda)^2} \tag{6}$$

quand on remplace λ par λ_1 et λ_2 racines de l'équation:

$$\lambda^2 - \mu(1-\eta)\lambda - \eta = 0 \tag{7}$$

Presque simultanément d'ailleurs H. Kuhn (8) et Taylor (9) proposaient la formule:

$$\delta^2 = Na^2\,\frac{1+\mu}{1-\mu}\,\frac{1+\eta}{1-\eta} \tag{8}$$

valable seulement pour les valeurs de η qui ne sont pas très voisines de l'unité et dont la formule 3 représente une approximation immédiate.

Les formules 5, 6, et 7 résolvent donc entièrement le problème tandis que les formules de Sadron (pour η voisin de zéro ou de l'unité), H. Kuhn et Taylor (pour η non voisin de l'unité) représentent des approximations que l'on retrouve d'ailleurs à partir des équations 5, 6, et 7.

Nous croyons utile de montrer comment les résultats approchés donnés par l'équation 8 s'écartent des résultats exacts. Pour cela nous représenterons, pour différentes valeurs de N, les valeurs de δ/a calculées en fonction de η par les deux formules (Figs. 2 et 3).

Le domaine de validité de l'équation 8 s'étend au fur et à mesure que N augmente mais il reste évident que lorsque η tend vers l'unité, la valeur δ^2 donnée par l'équation 8 tend vers l'infini et non pas vers L^2 carré de la longueur finie du zig-zag planaire.

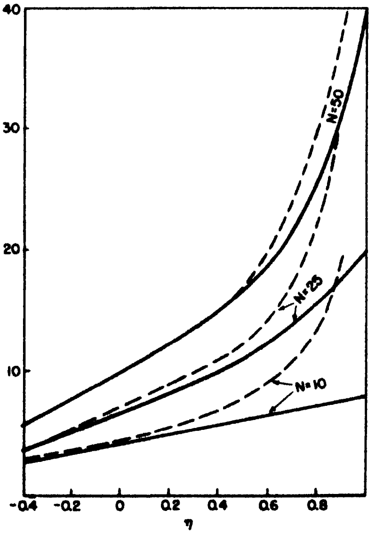

Fig. 2. Valeurs de δ/a en fonction de η pour N = 10, 25, et 50; —— formule rigoureuse, --- formule approchée.

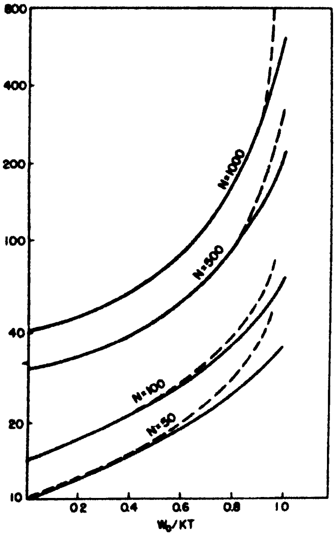

Fig. 3. Valeurs de δ/a en fonction de η pour N = 50, 100, 500, et 1000; ——formule rigoureuse, --- formule approchée.

Pour illustrer cette discussion nous donnons cidessous la formule 9 qui n'est qu'une autre manière d'écrire les formules 6,7 et 8:

$$\frac{\delta^2}{a^2} = N\frac{1+\mu}{1-\mu}\,\frac{1+\eta}{1-\eta} + \frac{2}{(1-\mu)^2(1-\eta)^2}\Big\{[2\eta + \mu(1+\eta^2)](\eta D_{N-1} - 1) + [\mu^2(1-\eta) + \eta(2\mu+1) + \eta^2]D_N\Big\} \tag{9}$$

D_N et D_{N-1} étant respectivement égaux à:

$$\frac{\lambda_1^N - \lambda_2^N}{\lambda_1 - \lambda_2} \quad \text{et} \quad \frac{\lambda_1^{N-1} - \lambda_2^{N-1}}{\lambda_1 - \lambda_2}$$

Le développement de δ^2 en fonction de $1 - \eta$ est alors:

$$\frac{\delta^2}{a^2} = N^2\,\frac{1+\mu}{2}\left\{1 - (1-\mu)\left(\frac{N}{6} - \frac{3}{2N}\right)(1-\eta) + \dots\right\} \tag{10}$$

Enfin, avant d'en terminer avec ce chapitre nous remarquerons que pour des valeurs de N assez grandes l'équation 5 ou 8 se met sous la forme:

$$\delta^2 = b^2 N \tag{11}$$

avec:

$$b^2 = a^2\,\frac{1+\mu}{1-\mu}\,\frac{1+\eta}{1-\eta} \tag{12}$$

Pour une chaîne de Gauss nous savons que la probabilité pour que l'écart entre les extrémités soit compris entre r et r + dr est donnée par la formule:

$$P(r)dr = \frac{1}{\lambda^3}\left(\frac{3}{2\pi}\right)^{3/2} 4\pi r^2 e^{-3r^2/2\lambda^2}\,dr \tag{13}$$

avec:

$$\delta^2 = \bar{r}^2 = \int_0^\infty r^2 P(r)dr = \lambda^2$$

On pourra que, donc dès que la formule 11 est appliciable, la loi de répartition de la distance entre les extrémités de la chaîne est donnée par la formule 13 où l'on fait $\lambda = \delta^2$. On retrouve ainsi le résultat déjà donné par W. Kuhn (3) et par Guth et Mark (2) pour les chaînes à rotations libres.

CALCUL DE η À PARTIR DE LA FONCTION DE RÉPARTITION W(B) DE L'ÉNERGIE

Dans nos travaux antérieurs nous avions admis que la répartition de l'énergie présentait un minimum pour la position "trans" et que l'on pouvait en première approximation poser:

$$W = \frac{W_0}{2}(1 - \cos B) \tag{14}$$

Dans ces conditions l'un de nous a montré (1) que l'on a:

$$\eta = -i\,\frac{J_1\left(i\frac{W_0}{2KT}\right)}{J_0\left(i\frac{W_0}{2KT}\right)} \tag{15}$$

où $i = \sqrt{-1}$, K est la constante de Boltzmann, T la température absolue, J_0 et J_1 les fonctions de Bessel d'ordre 0 et 1.

Mais H. Kuhn (8) et surtout Taylor (10) ont considéré un cas plus général et sans doute plus près de la réalité en admettant que la répartition de l'énergie W en fonction de B, tout en restant symétrique, présente trois barrières de potentiel: l'une pour B = π les deux autres pour B voisin de $\pm\pi/3$. C'est ainsi que Taylor pose:

$$W(B) = \frac{W_0}{2}\left\{X(1 - \cos B) + (1 - X)(1 - \cos 3B)\right\} \qquad (16)$$

$$0 \leqslant X \leqslant 1$$

Pour X = 1 on retrouve la répartition définie par l'équation 14, fig. 4a, pour X = 0 on trouve 3 barrières de potentiel égales (fig. 4b) et pour 0 < X < 1 on a le cas intermediaire illustré par la figure 4c pour X = 0.5. La valeur de η dépend alors de W_0 et X et peut être calculée par la statistique de Boltzmann. La figure 5 donne les valeurs de η en fonction de W_0/KT pour X = 0.2, 0.5, 0.8, et 1. Il faut remarquer que lorsque les 3 barrières de potentiel sont égales, le coefficient η est nul quel que soit W_0/KT.

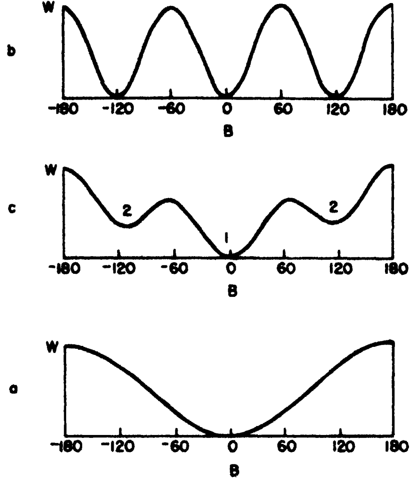

Figure 4

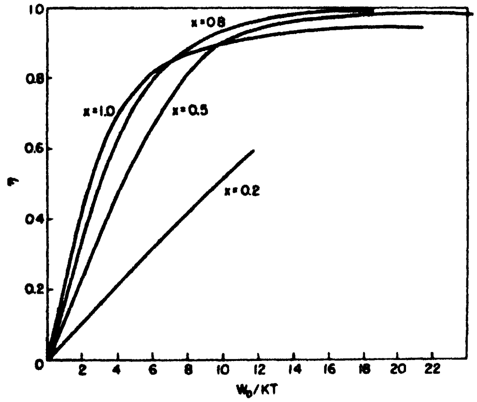

Figure 5

CALCUL DE δ^2

Connaissant ainsi les valeurs de δ^2 en fonction de η d'une part et celles de η en fonction de W_0/KT et X définissant la répartition de l'énergie, il est possible de calculer δ^2 en fonction de ces deux paramètres. C'est ce qu'ont fait Taylor et H. Kuhn de façon approchée, ainsi que nous l'avons vu. Les résultats rigoureux obtenus à partir des formules exactes, et les résultats approchés sont donnés par les figure 6 et 7 où nous avons porté les valeurs de δ/a en fonction de W_0/KT pour différentes valeurs de N dans les deux cas où X = 1 et X = 0.5.

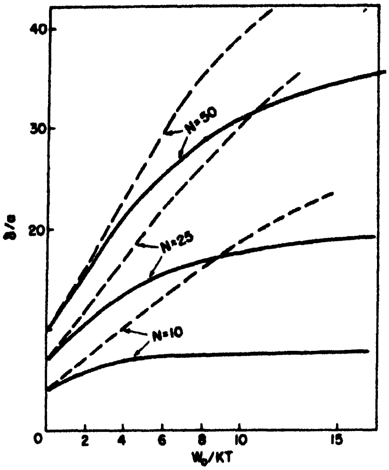

Fig. 6a. Valeurs de δ/a en fonction de W_0/KT pour N = 10,25, et 50 (X = 1); —— formule rigoureuse, --- formule approchée.

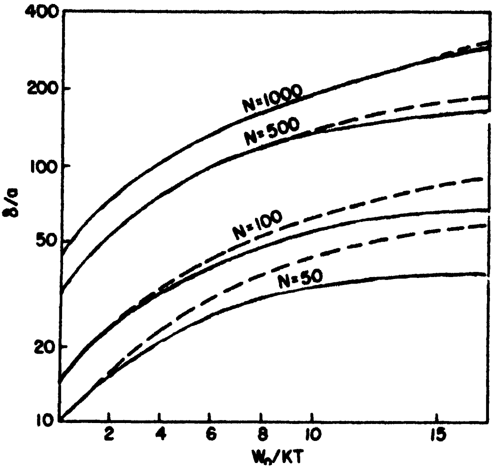

Fig. 6b. Valeurs de δ/a en fonction de W_0/KT pour N = 50,100,500, et 1000 (X = 1); —— formule rigoureuse, --- formule approchée.

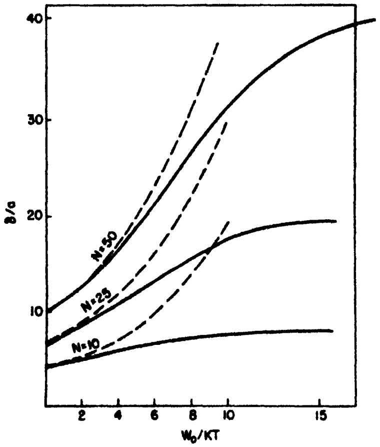

Fig. 7a. Valeurs de δ/a en fonction de W_0/KT pour N = 10,25, et 50 (X = 0.5); —— formule rigoureuse, --- formule approchée.

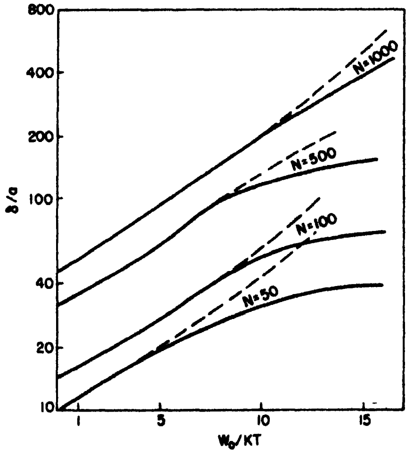

Fig. 7b. Valeurs de δ/a en fonction de W_0/KT pour N = 50,100, 500, et 1000 (X = 0.5); —— formule rigoureuse, --- formule approchée.

Ces figures permettent de déterminer facilement le domaine de validité des formules approchées. Avant d'en terminer nous désirons présenter quelques remarques sur les conséquences pratiques de la formule précédente.

1. Pour obtenir les valeurs numériques de δ^2 il est nécessaire de connaître les valeurs de W_0 et X. Taylor et H. Kuhn utilisent les

données de Pitzer (11) obtenues sur les carbures aliphatiques normaux par l'étude des spectres d'absorption infrarouge et des coefficients thermodynamiques des vapeurs. Nous ne pensons pas que cette manière de voir soit correcte car ainsi que nous l'avons signalé plusieurs fois W_0 est fonction de la nature du solvant employé et d'autant plus grand que meilleur est le solvant.

2. On peut relier la valeur de δ^2 à celle de la viscosité intrinsèque de la solution, ainsi qu'à celle de sa constante de diffusion brownienne en employant une méthode de "particule équivalente" développée par divers auteurs et en particulier par l'un de nous (12). Rappelons seulement que la méthode de la particule équivalente appliquée aux variations de la viscosité et de la constante de diffusion de translation en fonction de la température et du degré de polymérisation N permet en principe de déterminer W_0 et X.

3. Il convient de remarquer que l'on a admis implicitement jusqu'ici que le facteur W_0 est indépendant de N et de T et ne dépend que du solvant. Cette hypothèse constitue une approximation dont la validité reste à établir.

En effet le calcul de δ^2, tel qu'il a été conduit, ne fait intervenir que les interactions entre les chaînons d'ordres i et i + 2. Or ainsi qui l'ont fait remarquer de nombreux auteurs et tout récemment Simha (13) l'encombrement des atomes constituant la chaîne empêche celle-ci de prendre les configurations fortement pelotonnées qui seraient possible pour un squelette sans épaisseur.

Il s'en suit que pour la chaîne réele δ^2 doit être supérieur à la valeur calculée ci-dessus et ceci d'autant plus que η est plus petit.

On peut donc essayer de tenir compte de cet effet en ajoutant au terme W envisagé ci-dessus, un terme supplémentaire W_1 pouvant etre a priori fonction de N et de T.

De plus une deuxième raison a été signalée par l'un de nous (12): Si l'on admet que l'on puisse, en moyenne, délimiter la région de l'espace où se trouve la chaîne par une surface fermée (fig. 8) on peut

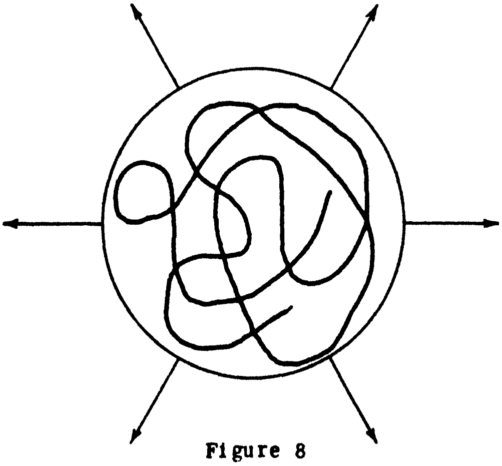

Figure 8

distinguer l'extérieur, constitué par du solvant pur et l'intérieur, constitué par une solution des N chaînons de la chaîne. Comme la surface fermée joue approximativement le rôle d'une surface limite entre la solution et le solvant il doit s'exercer sur cette surface des tensions dirigées de l'intérieur vers l'extérieur. En effet, on peut admettre que les chaînons qui se trouvent à la surface limite sont soumis en moyenne à une attraction provenant de l'extérieur (solvant pur) supérieure à celle qui provient de l'intérieur, (solvant contenant les chaînons). A cette tension supplémentaire devra donc correspondre un terme supplémentaire à ajouter à W_0 et W_1. Ce terme dépend de N et de T.

4. Enfin nous désirons attirer l'attention sur certaines conséquences de ce qui précède relativement à la précipitation des chaînes à partir de leurs solutions.

Cette précipitation peut être accomplie par deux procédés différents: abaissement de la température de la solution où adjonction d'une précipitant.

Il est clair que ces deux procédés ne sont pas équivalents et conduisent à des résultats différents. Supposons en effet que nous abaissons considérablement la température d'une solution très étendue.

Admettons tout d'abord que W(B) soit du type simple donné par l'équation 14. L'effet du refroidissement sera d'augmenter W_0/KT, donc de tendre chaque chaîne en zig-zag planaire. Si cet effet est obtenu au moment de la précipitation, les particules du précipité seront vraisemblablement constituées par la juxtaposition de ces zig-zag planaires en couches parallèles. Elles présenteront ainsi l'aspect d'un petit cristal fortement anisotrope. Admettons maintenant qu'il existe des barrieres de potentiel du type de la figure 5c. Lorsque la température est suffisamment basse l'agitation thermique est insuffisante pour que les barrières de potentiel puissent être franchies et dans ce cas la forme limite de la chaîne n'est plus un zig-zag planaire. La configuration de la chaine est obtenue en supposant que l'on ait n_1 atomes C_i dans les creux 1 (fig. 4c), et $2n_2$ dans les creux 2. En supposant que tous les creux 1 se trouvent à un bout de la chaîne et tous les creux 2 à l'autre bout on obtient: $\delta^2 = 0.66a^2(n_1^2 + 2n_2)$ En supposant au contraire que la répartition est régulière on obtient la formule approchée:

$$\delta^2 = a^2 \frac{7}{27} \frac{n_1^2}{n_2}$$

avec $\mu = 1/3$.

Il est vraisemblable que la valeur correspondant à une répartition au hasard est comprise entre ces deux valeurs. Et en appliquant la statistique de Boltzmann et les résultats déjà cités de Taylor:

$$\frac{n_1}{n_2} = \exp \frac{W_0}{2} \left\{ 1 - \frac{1}{3} \frac{(3 - 4X)^{3/2}}{(3 - 3X)^{1/2}} \right\}$$

Dans ce cas il se peut que les particules du précipité présentent un aspect cristallin moins net que si la chaîne se tend en zig-zag planaire (X = 1).

Supposons maintenant que nous ajoutions un précipitant dans la solution maintenue à température constante. L'effet de l'opération est de diminuer W_0, c'est à dire de faciliter l'agitation thermique jusqu'à ce que les rotations soient pratiquement libres. Si cet effet est obtenu au moment de la précipitation celle-ci ne fournit plus de particules cristallisées mais un floculat ayant l'aspect d'un gel.

then, the higher the degree of cross-linking the lower the elongation at which *some* of the chains become sufficiently oriented to undergo crystallization. Such crystallization increases the effective degree of cross-linking (14) of the chains involved and consequently the degree of crystallinity increases more rapidly with further elongation of the sample. The ultimate degree of crystallinity is rapidly attained, the retractive force rises steeply and rupture occurs at an elongation which may be related, qualitatively at least, to the elongation for incipient crystallization. Therefore, as the degree of cross-linking increases, both the elongation for incipient crystallization and the ultimate elongation decrease in roughly parallel fashion.

The relationship between the orientation of the network structure and the elongation may be approached from consideration of the action of an elongation on the set of "chain displacement" vectors, each of which leads from one cross-linkage to the next along the same chain. On stretching the sample, this set of vectors is distorted from a spherical to an ellipsoidal array. If the sample is stretched to the relative length α, it is readily shown that the fraction of the vectors elongated by the factor κ or greater is given by:

$$f_{\kappa} = 1 - [(\kappa^2\alpha - 1)/(\alpha^3 - 1)]^{1/2} \qquad (3)$$

which function only gradually approaches until with increase in α for a given value of $\kappa \geqq 1$. It is to be noted that f_{κ} is independent of the degree of cross-linking. Only those chains which are sufficiently oriented and elongated (the processes of orientation and elongation being mutually related) are potentially capable of participating in the formation of crystallites. The fraction of the chains meeting this requirement clearly will depend sharply on α. Hence, an increase in the degree of cross-linking lowers the elongation at which some of the structure may crystallize, but the fraction which is sufficiently oriented to participate in the formation of crystallites, even at the breaking elongation, is diminished[1]. According to the hypothesis that tensile strength is directly related to the fraction of the structure oriented sufficiently to allow it to participate in the formation of crystallites, the tensile strength should exhibit a corresponding decrease as the degree of cross-linking is increased, in accordance with observation at degrees of cross-linking beyond the maximum in the curve.

The increase in the tensile strength which accompanies rise in testing temperature up to about 100°C. according to certain results (15) cited by Gee (3) also may be explained on the basis of the above considerations. In accordance with the conclusion reached by Gee in this connection, an increase in temperature shifts the onset of crystallization to a higher elongation where a larger fraction of the chains are sufficiently oriented to undergo crystallization. Ultimate elongations were observed (15) to increase with the temperature also.

At higher degrees of cross-linking (i.e., beyond $\rho \times 100 = 3.0$ for the high molecular weight rubber) rupture presumably occurs before the onset of crystallization. In these higher vulcanizates the force of retraction rises rapidly with elongation in accordance with the theory of rubber elasticity (in the absence of crystallization) and may exceed the inherent strength of the material before it is reinforced by crystallization. This idea, mentioned previously by one of the authors (6), has been developed in considerable detail by Gee (3) who suggests it as the major factor responsible for the decline in the tensile strength beyond the optimum degree of cross-linking. In our opinion, however, it assumes importance only under conditions such that the observed tensile strength is very low, e.g., at degrees of cross-linking well beyond the maximum in the tensile strength curve, for very low primary molecular weights, or at temperatures (or dilutions) such that the tensile strength is only a few hundred pounds per square inch. The steep decline occurring near $\rho \times 100 = 3.0$ in the curve shown in Figure 2, and the corresponding intimation of a break in the curve of Figure 3, may be indicative of the degree of cross-linking beyond which crystallization on stretching vanishes.

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[1] The deformation of the residual noncrystalline polymer between incipient crystallization and ultimate rupture of the sample introduces a complication not considered above. The discussion given is intended to be qualitative only.

Effects of Foreign Units on Tensile Strength

The results obtained with the ethyl azodicarboxylate modified vulcanizates (Table IV; also shown in Figure 2) demonstrate that modification of up to 7% of the isoprene units with a substituent which is three times the size of the isoprene unit reduces the tensile strength relatively little. Previous emphasis (3,6) on the influence of small percentages of foreign units on the crystallinity and hence on the tensile strength appears to be unwarranted. Some other explanation is required for the decrease in tensile strength of vulcanizates from butyl rubber having 1.0 or more mole per cent of diolefin as compared with vulcanizates from butyl polymers having half this proportion of the unsaturated unit (6). Likewise, it now appears highly unlikely that the tensile strength of rubber vulcanized with sulfur and an accelerator is materially affected either by cyclization or by non-cross-linking reactions with sulfur, as has been suggested by Gee (3).

According to recent investigations into the nature of crystallization in polymers and copolymers, (16,17) introduction of foreign units at random along the polymer chain will lower the temperature for incipient crystallization, or "melting point", but a large depression requires a correspondingly large proportion of the foreign unit; the effect of the foreign units in the polymer chain resembles that of an impurity on the melting point of a monomeric substance. The degree of crystallinity at a given temperature below the melting point is suppressed to a somewhat greater extent. The most decisive effect of an occasional foreign unit which is incapable of entering the crystal lattice is the limitation of the lengths of the crystallites which may be formed. In the light of these considerations, the observed behavior of the EAD modified vulcanizates suggests that crystallites of great length are unnecessary for the realization of high tensile strength, and, furthermore, that the actual degree of crystallinity is not of direct importance. The crystallites presumably enhance the tensile strength by "cementing" adjacent chains together laterally at various regions along their lengths. Approximately the same tensile strength apparently may be achieved through the participation of each chain of the copolymer (i.e., partially modified polymer) in a number of shorter crystalline regions as through the presence of a fewer number of long crystallites in the unmodified polymer. According to the present results this remains true despite the much smaller degree of crystallinity to be expected in the copolymer. Hence, it is the fraction of the chains of the network structure which are induced to enter into crystallite formation at one or more regions along their lengths which is important, rather than the actual degree of crystallinity. At sufficiently high degrees of modification of the chain units, the tensile strength may fall to a low value owing principally to depression of the melting point to the extent that little or no crystallization occurs on stretching.

The above conclusions are corroborated by the rather small effect of random copolymerization on the tensile strengths of high melting oriented polyamide and polyester fibers (18). Although the tensile strength generally decreases somewhat with increasing proportions of the comonomer, the capacity for exhibition of high tensile strengths by no means destroyed even in 1:1 random copolymers. The residual elongation of the fully drafted fibers is appreciably increased by copolymerization, however.

Over-Cure and Ageing in Rubber Vulcanized with Sulfur and Accelerators

When the curing period is prolonged in the conventional vulcanization of rubber, or if the vulcanizate is heat aged, the tensile strength passes through a maximum beyond which it decreases with further heating. In the light of the above results, this decrease in tensile strength, commonly referred to as "overcure," cannot be attributed to modification of the chain units as suggested by Gee (3). The continued formation of cross-linkages or the occurrence of chain scission (or both) would, however, explain the observed decrease.

The "modulus," or force of retraction, of many compounds similarly passes through a maximum and then declines with further heating. According to the theory of rubber elasticity, the equilibrium force of retraction should be proportional to (19)

$$(1 - 2M/M_c) \cong (1 - 2/\rho\bar{x}_n)$$

The so-called phenomenon of "reversion" of the cure may therefore be due either to rupture of previously formed cross-linkages (a decrease in ρ), or to chain scission which causes M, and $\bar{x}_n$, to decrease. Simultaneous decreases in both tensile strength and "modulus" of highly cross-linked vulcanizates (i.e., beyond the maximum in Figure 2) indicates unambiguously, therefore, that chain scission takes place. Other changes, such as a decrease or increase in the degree of cross-linking, may of course occur simultaneously. It is to be noted that the elastic modulus and the tensile strength are affected differently by variation in $\bar{x}_n$, this being evident from the above expression and the discussion given in the preceding sections. Hence, characterization of the rubber by its force of retraction alone is inadequate.

Gee (3) has shown that two vulcanizates prepared from different compounds but cured for times such that they exhibit the same force of retraction at a given elongation will generally exhibit quite different tensile strengths. The lack of a direct correlation between tensile strength and modulus for rubber specimens vulcanized with different accelerators seems to be general, and it again points to the occurrence of differing degrees of chain scission.

While quantitative results are as yet quite limited, it is now clearly indicated that the apparently irrational dependence of various physical properties of vulcanized rubber on the complexities of the recipe and time of cure can be resolved logically in terms of two extremely simple structure variables: the degree of cross-linking and the primary molecular weight. A third variable, the degree of modification of the chain units, now appears to be of trivial importance, at least insofar as tensile strength is concerned.

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Synopsis

Tensile strengths of natural rubber samples quantitatively cross-linked with decamethylene dis-methyl azodicarboxylate have been determined. The proportion of the azo vulcanizing agent was varied 80-fold, the fraction p of cross-linked units in the products ranging from 0.10×10^{-2} to 8.0×10^{-2}. In spite of the small dimensions of the test specimen (cross section 0.10 in. by about 0.005 in.), the average error for a single observation is similar to that obtained in conventional testing procedures applied to specimens vulcanized with sulfur and

accelerators. Deviations from the mean for 262 tests on 15 different cures are well represented by a Gaussian error function; a slight intimation of skewness is evident only at the extremities of the distribtuion of deviations. These results are incompatible with the commonly held view that rupture of the sample takes place at the "weakest link" in the series of flaws inevitably occurring along the specimen. It would appear that the ability to withstand tensile stress (applied in a specified manner) is an inherent characteristic of the bulk material. The rapid increase in tensile strength with the degree of crosslinking ρ for small values of this quantity is consistent with the conclusion, previously reached in the investigation of the physical properties of butyl rubber (6) that the tensile strength is directly related to the fraction of the structure which is permanently oriented by stretching. At higher degrees of cross-linking (at $\rho \times 100 = 1.0$ to 1.5, depending on the molecular weight of the rubber) the tensile strength passes through a maximum and then declines steadily to quite low values for higher ρ's. This adverse effect of higher degrees of cross-linking is believed to result from the diminished elongation at which crystallization sets in and, hence, the smaller fraction of the network elements sufficiently oriented to participate in crystallite formation. Modification of up to 7% of the isoprene units of the rubber with the monofunctional compound, ethyl azodicarboxylate, depresses the tensile strength of the disazo vulcanized rubber relatively little. Evidently, the limited extent to which these modified (or copolymer) chains may enter into crystallization is adequate to bring about high tensile strength. Lack of direct correlation between modulus and tensile strength for rubbers vulcanized with various sulfur-accelerator combinations can only be explained by assuming that conventional vulcanization processes are accompanied to varying degrees by chain scission reactions. When vulcanized rubber is "over-cured," or heat aged, chain scission becomes excessive.

Résumé

La tension a l'étirement d'échantillons de caoutchouc naturel, quantitativement ponté par le dis-méthyl-azocarboxylate de décaméthylène, a été déterminée. La proportion d'agent vulcanisant a varié du simple à quatre-vingt fois sa valeur, la fraction ρ des unités pontées atteignant de 0.10×10^{-2} à 8.0×10^{-2}. Malgré les faibles dimensions de l'échantillon étudie (section de 0.10 in. sur 0.005 in.), l'erreur moyenne d'une observation determinée est semblable à celle obtenue dans les procédés conventionels appliqués aux échantillons vulcanisés au moyen de soufre et d'accélérateurs. Les déviations de la moyenne pour 262 essais sur 15 preparations différentes sont représentées par une fonction de Gauss; une légère tendance à la déviation est seulement évidente aux extrémités des distributions des déviations. Ces résultats sont incompatibles avec l' ideé généralement admise que l'échantillon se rompt a l'endroit de liaison plus faible, qui se presentent inévitablement sans un échantillon. Il semble que l'aptitude à résister à une force d'étirement soit une propriété caractéristique inhérente au materiel. L'accroissement rapide de la tension d'étirement avec le degré de pontage pour de faibles valeurs de celle-ci

est en accord avec la conclusion, antérieurement formulée dans les recherches sur les propriétes physiques du caoutchouc butylique (6), savoir que la tension d'étirement est directement liée à la fraction de la structure, qui est orientée de façon permanente par étirement. Aux degrés de pontages plus élevés (ρ x 100 = 1.0 jusque 1.5, suivant le poids moléculaire du caoutchouc) la tension d'étirement passe par un maximum, ensuite diminue constamment jusqu'a des valeurs notablement plus basses our des ρ plus élevées. Cet effet inverse des degrés de pontages élevés semble résulter de la diminution de l'élongation, à laquelle la cristallisation débute, et d'une quantité relative plus petite des élements du réseau, orientés suffisamment pour participer à la formation de cristallites. En modifiant les unités isopréniques jusqu'a 7% par un composé monofonctionnel, le azodicarboxylate d'éthyle, on ne provoque qu'une légère diminution de la tension à l'étirement de ces caoutchoucs, vulcanisés par le composé disazoique. Évidemment, la quantité limitée avec laquelle ces chaînes modifiées (ou ces copolymères) peuvent entrer en cristallisation, est favorable à l'obtention de forte tension à l'étirement. Le manque de corrélation directe entre le module et la tension à l'étirement pour des caoutchoucs vulcanisés avec divers mélanges soufre-accélérateur, peut uniquement être expliqué en admettant que les procédés habituels de vulcanisation sont accompagnés à des degrés variables, de réactions de scission de chaîne. Quand le caoutchouc vulcanisé est soumis à une préparation trop longue, ou vieilli à la chaleur, les ruptures de chaînes deviennent trop importantes.

Zusammenfassung

Die Zugfestigkeiten von Naturgummiproben, die quantitativ durch Decamethyl-Azocerboxylat vernetzt wurden, sind festgestellt worden. Das Verhaeltniss des Azo-Vulkanisationsreagenzmittels wurde 80 fach variiert, wobei die Fraktion vernetzter Ketten in den Produkten zwischen 0.10 und 10^{-2} lag. Obgleich der Pruefstab kleine Dimensionen hatte, (Querschnitt 0.10'' x 0.005'') war der Durchschnittsirrtum einer Einzelbeobachtung aehnlich dem, der unter konventionellen Pruefungsmethoden mit Schwefel und Beschleunigern vulkanisierter Proben erhalten wird. Abweichungen vom Durchschnitt fuer 265 Pruefungen und 15 verschiedene Aushaertungen werden durch die Gauss'sche Irrtumsfunktion gut dargestellt nur die Verteilung extremer Abweichungen ist etwas unsymmetrisch. Die Ergebnisse sind unvereinbar mit der haeufig vorkommenden Ansicht, dass der Bruch einer Probe im schwaechsten Gliede einer Serie von Fehlstellen, die unvermeidlicherweise in der Probe vorkommen, stattfindet. Man muesste annehmen, das die Faehigkeit, einem Zuge zu wiederstehen, (wenn er in einer gegebenen Weise angewandt wird) eine Eigenschaft des Stoffes ist. Die schnelle Zunahme an Zugfertigkeit mit dem Grade der Querverbindung fuer kleine Werte dieser Qualitaet ist mit dem Schlusse, der frueher in Untersuchungen physikalischer Eigenschaften von Butylgummi (6) gezogen wurde, vereinbar, dass naemlich die zugfestigkeit direkt von der Fraktion der Struktur abhaengt, die durch Dehnen permanent orientiert wird. Bei hoeheren Vernetzungsgraden (bei ρ x 100 zwischen 1.0 und 1.5 je nach dem Molekulargewicht des Gummis) geht die Zugfestigkeit durch einen Maximalwert

und verringert sich dann ununterbrochen bis zu ganz niedrigen Werten bei höhen ρ's. Dieser nachteilige Einfluss hoher Querverbindungsgrade ist wahrscheinlich eine Folge der verringerten Dehnung, bei der Kristallisation einsetzt, und demgemaess, der kleineren Fraktion der Vernetzen Glieder deren Orientierung gross genug ist, um sie an der Kristallisation teilnehmen zu lassen. Modifizierung bis zu 7% der Isoprenglieder von Gummi mit der monofunktionalen Verbindung Aethyl Azodicerboxylat drueckt die Zugfestigkeit des dis-azo vulkanisierten Gummis nur relativ wenig herab. Offensichtlich genuegt das begrenzte Ausmass, in dem diese modifizierten (oder Mischpolymerisat.) Ketten an der Krystallisation teilnehmen koennen, um höhe Zugfestigkeit sicherzustellen. Der Mangel an Korrelation zwischen Modul und Zugfestigkeit fuer Gummis, die mit verschiedenen Zusammenstellungen von Schwefel und Beschleunigern vulkanisiert wurden, kann nur durch die Annahme, dass konventionelle Vulkanisierungen von verschiedentlich weitgehenden Kettenspaltungsreaktionen begleitet sind, gedeutet werden. Wenn vulkanisierter Gummi "ueberhaertet" wird, oder bei hoher Temperatur gealtert wird, findet eine uebermaessige Kettenspaltung statt.

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Polyelectrolytes. V. Osmotic Pressures of Poly-4-vinyl-N-n-butylpyridonium Bromide in Ethanol at 25° *

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INTRODUCTION

The osmometer has been one of the standard tools of research in physical chemistry for well over a century (1). Theoretical interpretation began with van't Hoff's (2) treatment of Pfeffer's (3) data, which led to the well-known analogy between the behavior of molecules in solution and that of the same number of molecules in the same volume as gas. Deviations from ideal behavior for various real solutions were observed and eventually accounted for in a satisfactory way. Herzog and Spurlin (4) were pioneers in the study of the osmotic pressure of synthetic high polymers: they found that the osmotic pressure of benzyl cellulose solutions in methyl glycol acetate was linear in concentration below 1% of solute by weight, but that the deviations from ideal behavior were very large. Subsequent investigators (5,6) showed that this behavior was a general characteristic of substances of high molecular weight; using a model suggested by Meyer (7), Flory (8) and Huggins (9) independently showed that the deviations from ideality exhibited by polymers were due to entropy terms which arose from the many possible configurations which a chain molecule could assume in solution. We are now able to make reliable measurements of osmotic pressures of polymeric systems and to obtain the molecular weight of the solute from the data. Still more important, the variation of the osmotic coefficients with concentration and temperature can be correlated with the interaction of solute molecules with each other and with those of the solvent.

Electrolytes proved to be one of the major problems in the field of colligative properties of substances of low molecular weight; it was nearly half a century after van't Hoff's work that Debye and Huckel (10) finally succeeded in making a practical calculation of the effect of long range interionic forces on thermodynamic properties of electrolytic solutions. Likewise, in the field of substances of high molecular weights, electrolytic compounds present many unusual properties when contrasted with neutral polymers. One of the classical problems in this field is that of proteins (11), which are, of course, electrolytes of high molecular weight. Lillie (12) found that the osmotic pressure of gelatine solutions depended on the concentration of other electrolytes simultaneously present. Later the importance of the isoelectric point of proteins was understood, and Loeb (13) was able to account for the change of osmotic pressure of protein solutions with electrolyte concentration and pH by means of the Donnan (14) equilibrium. The protein situation is, however, complicated by the fact that the ionogenic groups of the protein, carboxyl and amino, are weak; hence dissociative equilibria must be considered in calculation.

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Compounds of the type we have described in earlier papers (15-17) of this series permit another approach to the problem of thermodynamic properties of polyelectrolytes. Polyvinylpyridine is a typical polymer, much like the familiar polystyrene. By the addition of alkyl halides, it can be converted into a strong polyelectrolyte of known molecular weight and structure. The fact that the resulting electrolyte is strong eliminates the difficulties due to the dissociation processes characteristic of weak acids and bases, including direct hydrolysis or membrane hydrolysis. Synthetic polyelectrolytes offer several other advantages over naturally occurring substances as research material: (a) they are stable; (b) their structure, within reasonable limits, can be varied at will; and (c), nonaqueous solutions can be studied. The significance of the first two points in obvious; the third will be essential in a general treatment of polyelectrolytes, because varying the solvent permits variation of dielectric constant, and it is this variable which controls the intensity of Coulomb forces which are, in last analysis, responsible for the properties which are peculiar to electrolytes. Our knowledge to date of the properties of polyelectrolytes is almost entirely limited to that of proteins, nucleic acids, and polysaccharides in aqueous solution. It is our hope that an investigation of the general field will lead to a better understanding of the special one.

The purpose of this paper is to present the results of a preliminary experimental study of the osmotic pressures of solutions in ethanol of polyvinylbutyl-pyridonium bromides of (number average) degrees of polymerization 730 and 1900. It is not possible yet to treat the general case of Donnan equilibria for strong polyelectrolytes in nonaqueous solvents, because association due to electrostatic interaction reduces free ion concentrations below the corresponding stoichiometric concentrations and because activity coefficients may not be approximated by unity as is frequently (although incorrectly) done in the case of aqueous solutions. We first consider, therefore, the case where polyelectrolyte is the only solute. Here, we have one of the limiting cases of the Donnan equilibrium where no diffusible electrolyte is present (except perhaps for small amounts of impurity) and the observed osmotic pressure is due to the polyions plus the counter-ions which, although small enough to pass through the membrane, are retained on the solution side of the cell by the condition of electrical neutrality. At a given concentration in the dilute range (hundredths of 1% by weight), we find that the osmotic pressure of the polysalt is over an order of magnitude greater than that of the parent polymer. This pressure is, however, very much lower than the limit which would correspond to zero association of counter ions to the polycations, whence we conclude that the polymeric ions carry with them a significant fraction of bromide ions, held solely by Coulomb attraction. By simultaneous measurement of conductance, an estimate of the transference number of the polyion can be made; we find about 0.3 for the sample of low molecular weight and 0.5 for that of high.

By the addition of a large excess of a simple one-one salt (lithium bromide) to the solution, we obtain another limiting case of the Donnan equilibrium where again the observed osmotic pressure is due to the nondiffusible polyelectrolyte. In this case, the association of gegenions to the polyion is markedly increased, as is demonstrated by the resulting sharp decrease in osmotic pressure. By measuring the osmotic pressure of a polyelectrolyte in solutions of a simple electrolyte as solvent, it may be possible to obtain the molecular weight of the polyelectrolyte by extrapolation to infinite ionic strength of added electrolyte (18,19). Further work is in progress.

EXPERIMENTAL

Materials

Polyvinylpyridine. 10 cc. of redistilled (18 mm., 68°) 4-vinylpyridine were diluted with 500 cc. toluene, and 1.0 g. benzoyl peroxide was added. The solution was deoxygenated at room temperature by evacuating until the liquid boiled and then admitting nitrogen; this step was repeated three times. The mixture (under nitrogen) was then placed in a shaking machine in a water bath at 40°. After 21 hours, 13.7 g. polymer (No. 421) was separated by centrifuging; 1.3 g. additional benzoyl peroxide was added, and after deoxygenation, the mixture was put back on the shaker for 8 days. The main lot of polymer (No. 422) was then centrifuged out. The supernatant liquid was completely colorless; presence of oxygen produces a yellow color. The polymer was twice washed with benzene, dried in vacuum, suspended in benzene and stirred for one hour, centrifuged, and finally dried in vacuum at 40° for several days. The total yield was 70.4 grams. Dumas nitrogen was 13.15%, 13.01%; theoretical 13.32%.

Viscosities were measured in ethanol solution; the following values were found; $C = 0.408$ g./100 cc., $\eta_{sp}/C = 2.04$; 2.13 at 0.532 g./100 cc.; 3.13 at 1.408 g./100 cc. Due to an error in estimation of quantities, the above data are not properly spaced for the conventional extrapolation plot for intrinsic viscosity $[\eta]$. Using the equation (20):

$$\eta_{sp}/C = [\eta] + k' [\eta]^2 C \tag{1}$$

with $k' = 0.35$, the value we obtained for other polyvinylpyridine (19) samples, we calculate $[\eta] = 1.64$ from the two data at low concentrations.

Polyvinyl-N-butylpyridonium Bromide. One sample of this compound was prepared from the polymer (No. 422) described in the previous paragraph by reaction in nitromethane solution at 55° with *n*-butyl bromide. We designate this as Salt 4115. Bromide was determined by potentiometric titration; found, 31.58%, 31.58%; theoretical, 33.00%. Dumas nitrogens gave 5.50%, 5.54%; theoretical, 5.78%. The bromide is 95.6% of theoretical and the nitrogen is 95.5% of theoretical, so we conclude that each nitrogen carries one ionic bromine. We are indebted to Mr. W. N. Maclay of this laboratory for these analyses.

A solution of Salt 4115 (0.602 g./100 cc. or 0.0237 equivalents bromide per liter) in water of pH 5.84 gave a pH of 3.18, which indicates that some side reaction occurred whereby hydrogen bromide rather than butyl bromide finally added to pyridine nitrogens. Assuming activity equal to concentration, a pH of 3.18 corresponds to a 6.6 x 10^{-4} normal solution of acid in the 0.0237 normal polysalt solution.

Another sample of salt (No. 612) was also studied. This was prepared from the polyvinylpyridine described in Part II of this series (15), which had a molecular weight of 77,000 (DP 730, about one third that of salt 4112).

Ethanol. Stockroom ethanol was redistilled and the density and specific conductance were measured. The latter varied from 0.043 x 10^{-6} to 0.073 x 10^{-6}, which was about 5% of that of the most dilute solution of polyelectrolyte studied.

Lithium Bromide Solution. We used Eimer and Amend C. P. lithium bromide, undried. A sample weighing 245 g. was dissolved in 92.5% ethanol, filtered, and made up to a total of 3109 g. with ethanol. Potentiometric titrations gave an average of 0.7104 moles lithium bromide per kilogram solution. From these data, we calculate that the final solvent was 90.9% ethanol. The density of the solution at 28.0° was 0.856; using the temperature coefficient of ethanol, this gives 0.858 for the density at 25°, whence we find that the solution was 0.610 normal in lithium bromide.

Apparatus

The osmometer used in this investigation was that described by Fuoss and Mead (21); we are indebted to the Research Laboratory of the General Electric Co., for the loan of this apparatus. It was equipped with water jackets (22), through which water, thermostated at 25.00° ±0.03, was circulated.

Membrane corrections were determined in the usual way, with solvent on both sides of the cell. One membrane was used for all the work herewith reported; its correction was 0.18 cm. for ethanol as solvent. With 0.610 N lithium bromide as solvent, the membrane correction was erratic during the first two hours after filling the osmometer; it then became steady at 0.24 cm. This value was reproduced on subsequent fillings. Diffusion of solvent through the membrane was about half as fast with the lithium bromide solutions as with the ethanol soluitions; readings were accordingly taken at 60 second, rather than at 30 second intervals.

In order to check the behavior of the osmometer, we frequently left solutions in the osmometer overnight. As previously pointed out (21). low molecular weight polymer will diffuse into the solvent cell on standing. But the dynamic reading taken the next morning, without changing contents of either half cell, always agreed with the static level which the system had arrived at during standing. Another convenient working check is the difference between levels for rising and falling meniscus, when the rate has reached a definite numerical value. For example, with our membrane and ethanol solutions, when the meniscus was rising at the rate of 0.080 cm./min., the level was always 0.88 cm. below the level at which it would fall at the same rate of 0.080 cm./min. (See Figure 3 of Reference 21.) Finally, we required that two successive fillings of the osmometer give the same dynamic osmotic pressure within 0.05 cm. Apparently, some polymer is adsorbed on the membrane because we found that the osmotic pressure came reproducible after two fillings, if these were allowed to stand in the osmometer at least one hour each. If successive portions of solution and solvent were introduced, measured, and drained in rapid succession, half a dozen or more fillings were necessary before reproducible readings were obtained.

With Polymer 421, the apparent osmotic pressure dropped about 10% on standing at least 5 hours, due to diffusion of material of low molecular weight to the solvent side. Replacement of the liquid in the latter side by fresh solvent always brought the level half-way back to the initial value, in accordance with our earlier observations. We attempted to determine the actual weight of the diffusible material. In one experiment, a solution (1.44 g./100 cc.) gave an initial osmotic pressure of 6.56 cm., which dropped to 6.04 cm. on standing overnight, a decrease of nearly 10%. The contents (20 cc.) of the solvent half-cell were then drained into previously weighed weighing bottle and the liquid was carefully evaporated. No detectable residue was found; i.e., certainly less than 0.5 mg. were responsible for the 0.52 cm. drop in osmotic pressure. The solution half-cell contains 20 cc., of which half is in contact with the membrane; hence about 0.144 g. whole polymer were originally present in the solution half-cell adjacent to the membrane. To give a 10% decrease in osmotic pressure, the less than 0.5 mg. (0.3% of whole polymer) could not possibly have had a molecular weight greater than 3000. Actually, the value was probably much lower than this, because 0.5 mg. is a very liberal estimate of weighing error; had we taken 0.1 mg., for example, the upper limit would have been only 600. The impurity might have been benzoic acid from the catalyst. In any case, this observation suggests that osmotic pressures obtained after dialysis of the sample are more representative of the polymer than are those obtained by the dynamic method shortly after filling the osmometer.

The most convenient units for practical laboratory work are pressures π in centimeters of solvent and concentrations w in grams of solute per kilogram solution. In these units, the limit of (π/w) at zero concentration is $1033\,RT/M = 25{,}280/M$, where M is the number average molecular weight. In conventional units (p in g./cm.^{2}, and C in g./100 cc.), the ratio p/C is simply $10\,\pi/w$ because the density appears in both numerator and denominator on converting units ($w = 10\,C/\rho$; $\pi = p/\rho$).

RESULTS

The osmotic pressures of Polymer 421 are given in Table I. The second column gives π_0, the initial dynamic value of the osmotic pressure, and includes the contribution due to diffusible impurity. On standing, the osmotic pressure drops to ($\pi_0 - \delta\pi$); on refilling the solvent half-cell with fresh solvent, the dynamic pressure measured immediately rises to ($\pi_0 - \delta\pi/2$). On standing, the pressure again drops to (π_0 - $\delta\pi$) as half of the remaining material of low molecular weight diffuses out of the solution half cell. Repetition of this process gives a final dynamic and static osmotic pressure π_∞ = (π_0 - $\delta\pi$). The values of π_∞ are given in the third column of Table I; it will be noted that (π_0 - π_∞) is proportional to w, as should be the case if the drop is due to a fixed percentage of diffusible impurity.

TABLE I. Osmotic Pressures of Polymer 421 in Ethanol at 25°

w	π_0	π_∞	C	p_0/C	p_∞/C
3.03	0.54	0.48	0.243	1.78	1.58
5.64	1.27	1.12	0.452	2.25	1.99
8.07	1.94	1.76	0.648	2.40	2.18
9.43	2.49	2.27	0.756	2.64	2.41
17.94	6.35	5.86	1.440	3.54	3.27

The data are linear on the conventional plot of pressure over concentration versus concentration; the open circles of Figure 1 correspond to p_0/C and the solid ones to p_∞/C. The former extrapolated to M = 165,000 and the latter to M = 195,000. As explained in the previous section, we believe the latter figure to be more accurately descriptive of the polymer. Polymer 422 was not significantly different from No. 421. Two solutions with C = 0.953 and 0.556 g./100 cc. gave p_∞/C = 2.72 and 2.35, respectively; these values are to be compared with 2.65 and 2.08, the values interpolated from Figure 1 for No. 421 at the same concentrations. The density of a pressed disk of polyvinylpyridine was found to be 1.153 g./cc. Using this value, and the slope 1.43 of the p/C - C plot, we find μ = 0.464.

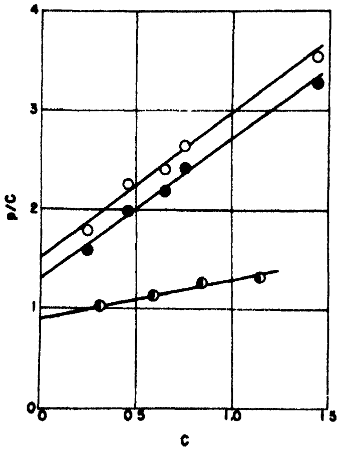

Fig. 1. Osmotic Pressures. Open circles, initial values for Polymer 421; solid circles, final values; half-black circles, Salt 4115 in 0.610 normal alcoholic lithium bromide solution.

As might be expected, the polyelectrolytes gave a much higher osmotic pressure at a given weight concentration than the corresponding parent polymers, due to the effect of the counter ions. For example, the average degree of polymerization of Salt 4115 is approximately 1900; if no association occurred, the number of particles from a given weight of the salt would be 1901 times those from the same weight of polymer; 1900 bromide ions and one polycation. Actually, the pressures were only between 10 and 100 times as large as that of the polymer, indicating a rather high degree of association of counter ions to polycations.

The behavior on standing in the osmometer of the polyelectrolytic solutions was markedly different from that of solutions of electrically neutral polymers. On standing overnight, the apparent osmotic pressure dropped from 20 to 35% of the dynamic value obtained at "zero" time (as soon as temperature equilibrium was established after filling). But on refilling the solvent half-cell with fresh solvent, the pressure rose much more than half the drop. Our tentative explanation is that hydrogen bromide was responsible. (We recall that the salt gave a slightly acid solution in water.) Pyridine is a very weak base and in solution, most of the hydrogen bromide would be free to diffuse through the membrane. We have here a case of Donnan equilibrium where a small amount of diffusible electrolyte is present with a large excess of nondiffusible electrolyte, and where practically all of the diffusible electrolyte is driven through the membrane, where it then exerts a large counter pressure. On refilling the solvent half-cell, the osmotic pressure rises nearly to that corresponding to the polysalt alone. The magnitude of this effect is shown in Table II where π_0 and π_∞ have the same significance as before, while π' is the dynamic (and static) value found for the initial filling of the cell after it had remained in the cell for at least 6 hours but before refilling the solvent half-side of the cell. It will be noted that ($\pi_0 - \pi'$) is linear in w, corresponding to a constant percentage of diffusible electrolytic impurity. The values of ($\pi_0 - \pi_\infty$) for the polysalt are much smaller than for the parent polymer; presumably, most of the impurity of low molecular weight in the latter was extracted during the preparation of the salt from the polymer.

TABLE II. Variation of Osmotic Pressure Due to Dialysis

w	π_0	π'	π_∞	π_∞/π_0
		Salt 4115		
0.195	0.58	0.37	0.51	0.880
0.242	0.70	0.48	0.63	0.900
0.334	1.03	0.72	0.91	0.884
0.863	2.46	1.96	2.34	0.952
1.309	3.66	2.93	3.61	0.986
1.779	4.65	3.81	4.43	0.953
2.460	6.60	5.29	6.48	0.982
		Salt 612		
0.177	0.70	0.48	0.64	0.915
0.322	1.34	1.02	1.21	0.904
0.582	2.49	2.02	2.32	0.932
0.863	3.48	2.86	3.19	0.916
1.583	6.18	5.12	5.77	0.934

The membrane correction of 0.18 cm. has been applied to all the data of Table II. As will be shown later in the discussion, there is some doubt concerning the proper value of membrane correction to be used in the presence of ions; there are indications that it varies with electrolyte concentration, and further study is needed.

TABLE III. Conductances of Polyelectrolytes in Ethanol at 25°

10^3c	Λ	10^3c	Λ
	Salt 4115		
Series 1		Series 3	
0.3108	3.93_8	0.621	3.75_1
0.7416	3.69_6	0.769	3.75_6
3.604	3.31_3	1.062	3.66_8
13.093	2.89_2	1.721	3.55_3
Series 2		2.745	3.46_2
16.14[a]	2.766	4.165	3.32_8
68.96	1.997	5.660	3.24_7
258.4[b]	1.433	7.827	3.12_4
	Salt 612		
0.563	3.70_3	2.751	3.12_4
1.027	3.43_3	5.046	2.92_9
1.854	3.25_7		

[a] $\eta/\eta_0 = 1.65$

[b] $\eta/\eta_0 = 9.55$; $\rho = 0.833$

Conductances were also determined using the same apparatus and technique as before (16). In discussion of conductance data, weight concentrations (C or w) are meaningless, and it is therefore necessary to refer the data to concentrations c, expressed as stoichiometric equivalents of bromide ion per liter. The relation between the three concentration scales is given by:

$$c = 10C/m = \rho w/m \tag{2}$$

where ρ is density and m is the equivalent weight of a monomer unit. In Table III, we give the equivalent conductances Λ of the salts, which were calculated from the observed total[1] specific conductances κ by the usual definition:

$$\Lambda = 1000\ \kappa/c \tag{3}$$

In Series 1, the density of the alcohol was 0.8041, corresponding to 93.5% ethanol, and the solvent conductance was 0.067×10^{-6}. The corresponding figures for Series 2 and 3 and for Salt 612 are: 0.8052, 93.1%, 0.073×10^{-6}, 0.8072, 92.4%, 0.043×10^{-6}; and 0.8066, 92.6%, 0.048×10^{-6}. Different lots of alcohol had slightly different ethanol contents, and hence different viscosities and dielectric constants;

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[1] For discussion of solvent correction, see page 253 of reference (15).

effects of these variations are not pertinent to the present discussion. Approximate viscosities of two of the most concentrated solutions were measured; it will be noted that the relative viscosity increases very rapidly with concentration, reaching nearly 10 in a 6.5% solution.

In order to determine the effect of the presence of excess simple electrolyte on the properties of the polymeric electrolyte, both osmotic pressures and conductances of Salt 4115 were measured in 0.610 normal lithium bromide solution as solvent. The data are summarized in Table IV. It was noted that the osmotic pressures were always somewhat erratic for an hour or so after replacing solvent in the solution half-cell with solution, but steady reproducible values were obtained after about two hours. The π_0 figures of Table IV therefore refer to data taken after this time. On standing overnight, the osmotic pressure remained constant or else increased somewhat. This observation supports our guess that the large decrease and subsequent large regain for the polyelectrolyte alone (Table II) were mostly due to hydrogen bromide, because the small amount of this impurity would be invisible in the presence of the large excess of lithium bromide. It will be noted that the p/C values (averaged over π_0 and π_∞) are of the same order of magnitude as those of the neutral polymer. In the fifth column of Table IV are given the specific conductances of the solutions and in the last, the decrease in specific conductance produced by the addition of polyelectrolyte to the lithium bromide solution.

TABLE IV. Properties of Salt 4115 in 0.610 N Alcoholic Lithium Bromide Solution

C	π_0	π_∞	p/C	$10^3\kappa$	$-10^3\Delta\kappa$
0.000	-	-	(0.90)	7.563	0.000
0.312	0.34	0.41	1.02	7.541	0.022
0.586	0.77	0.77	1.13	7.510	0.053
0.846	1.22	1.27	1.26	7.448	0.115
1.147	1.75	1.75	1.31	7.447	0.116

From the specific conductance of the lithium bromide solution used as solvent, we calculate $\Lambda = 12.40$ for lithium bromide at 0.610 normal in ethanol. By Walden's rule we estimate Λ_0 for this salt to be 82.5; hence there is also considerable ion association of the univalent ions in this solvent.

DISCUSSION

It is first necessary to comment on the membrane correction for the data on the polyelectrolytes. We found 0.18 cm. with ethanol on both sides of the membrane, and 0.24 cm. with 0.610 N lithium bromide solution on both sides. In Figure 2, we have plotted the p/C data for both polymeric salts; the upper curve for each salt gives the data based on π_0 values (cf. Table II) without membrane correction and the lower curve gives the p/C values based on π_0, using a membrane correction of 0.18 cm. As might be expected, there is no significant difference at higher concentrations. But in the range of low concentrations, the corrected curve for Salt 4115 is considerably flattened, and for Salt 612, a maximum around 50 mg./100 cc. appears. The latter certainly is fictitious because the limit at zero concentration for p/C must be approximately[1] 1000 and the curve must necessarily be concave-upward. It thus appears that 0.18 cm. is an over-correction for membrane assymetry and we shall disregard the correction for the present.

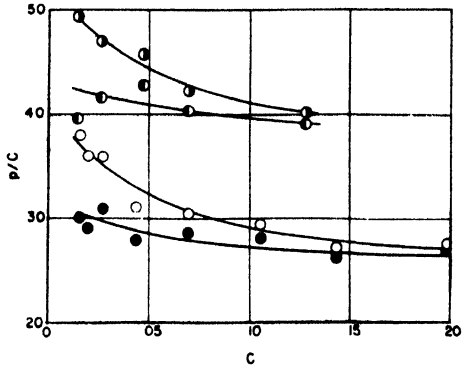

Fig. 2. Osmotic pressures of polyelectrolytes. Right-black circles, Salt 612, uncorrected initial values; left-black circles, Salt 612, corrected initial values. Open circles, Salt 4115, uncorrected initial values; solid circles, Salt 4115, corrected initial values.

One other source of error must be mentioned: the small increment $\Delta\pi$ of osmotic pressure ($\pi_0 - \pi_\infty$) which we tentatively ascribe to residual impurities. Again, this error becomes negligible at higher concentrations, but affects the shape of the curve at low concentrations. As seen in Table II, $\Delta\pi$ is approximately constant, and its effect is obviously one which increases with decreasing concentration on a p/C plot. Since the conductance data necessarily include contributions from electrolytic impurities, we shall use the π_0 values for comparisons between these two sets of data.

Regardless of these two uncertainties, three significant differences between the p/C curves for the polyelectrolytes and those of the parent polymers are obvious, on comparing Figures 1 and 2. First, the magnitude of the osmotic pressure of the polyelectrolytes is by far greater; for example, at 0.2 g./100 cc. (the highest concentration measured for the polysalt and the lowest for the polymer), the p/C values are, respectively, 28 and 1.8. Second, the osmotic pressure-concentration ratio of the polysalt increases with dilution while that of the polymer decreases. Third, the p/C - C plots are linear for the polymer and curved for the polyelectrolyte. These characteristics are, of course, to be expected for a salt of the type under consideration. The osmotic pressure is high, because each free bromide ion which is not bound to (or in) a polycation by Coulomb forces contributes just as much to osmotic pressure as a single macromolecule. As dilution increases, more and more bromide ions escape from the electrostatic fields of the large positive ions, and the osmotic pressure increases correspondingly. Finally, since electrostatic forces are involved, linearity in the first power of concentration is not to be expected, because neither concentrations of free ions nor activity coefficients are linear in concentration.

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[1] In the hypothetical limit of zero concentration, no bromide ions would be associated with the polycation; hence a polysalt with degree of polymerization n would give (n + 1) particles, and the limiting osmotic ratio would be $(p/C)_0 = 2.53 \times 10^5/(1/m + 1/M) \approx 2.53 \times 10^5/m$, where m is the molecular weight of the monomer unit. Since m = 242.2, and the compound analyzed to 95.2% theoretical bromide, the effective monomer weight is then 242.2/0.952 = 254. Practically, this limit cannot be reached because at any low but finite concentration, the positive field of the polycation is enormous, and a certain number of anions will be associated with the cations. In other words, the solution will act as if to each molecule of polyelectrolyte, there corresponded (n - m + 1) particles, where m changes only extremely slowly with concentration. A similar paradox has been discussed for the case of conductance; cf. p. 257 of Ref. (15).

Dissociation of the polyelectrolyte in alcohol is far from complete, as in evident from the disparity between 1000, the theoretical limit of p/C and the observed values of 30-50. Even at this range of dielectric constant, however, it is interesting to note that the salt of lower molecular weight gives the higher osmotic pressure (cf. Figure 2) at a given weight concentration. It should be emphasized that this is not due to the same cause which operates in the case of neutral materials, where a given weight contains more (whole) molecules of material of lower molecular weight. Rather, the higher osmotic pressure of the polyelectrolyte of lower molecular weight is due to the greater number of bromide ions free at a given concentration due to its relatively weaker electrostatic field. In other words, the Coulombic binding capacity for bromide ions is greater if a given weight of polycation is present as fewer, but larger more highly charged units.

When an excess of simple one-one electrolyte is added to the polysalt, we would expect a marked decrease in osmotic pressure because the excess of counter ions would in the limit completely suppress the dissociation of the polyvalent electrolyte. As shown in the lower curve of Figure 1, this is precisely what happens when 0.610 normal lithium bromide solution is used as the solvent for Salt 4115. The osmotic pressure is depressed below that of the parent polymer and the curve is now linear, extrapolating to an intercept of 0.90, with a much smaller slope (larger μ value) than that of the neutral polymer in ethanol. If, on the average, one free bromide ion were present for each molecule of polyelectrolyte, the p/C intercept for the polysalt in lithium bromide solution would be a little lower than 1.30, that for the parent polymer; 1.30 x (105)/(242/2) = 1.13. If suppression were complete, the intercepts for Polymer 421 and Salt 4115 should be in the inverse ratio of the weights of the monomer units, 242/105 = 2.30, which would correspond to an intercept of 0.57 for the salt. Actually, they are in the ratio 1.30/0.90 = 1.45, indicating that on the average less than one free bromide ion is present per molecule of polyelectrolyte. It will be interesting to study the osmotic pressures of polyelectrolytes in different concentrations of added salt, to see if an extrapolation to "infinite concentration" of added electrolyte will give the molecular weight of the polyelectrolyte, in analogy to our result for viscosity (18). We also plan to study the dependence of the slope on concentration and type of added electrolyte.

The conductance curves for the two salts (612 and 4115) are shown in Figure 3. For comparison, our previous data (15) for another sample of electrolyte (Salt II) prepared from the same parent polymer as Salt 612 are also shown. The curve for Salt 612 is lower by about 10% and not quite parallel to the previous curve; we can offer no explanation for this discrepancy. More experience in preparation and purification of salts is obviously needed. One significant difference between Salts 612 and 4115 appears: in our working range of concentrations, Salt 4115 shows a marked curvature on a log Λ - log c plot, while the data for Salt II give a linear plot. The log Λ - log c plot must eventually become concave to the concentration axis for all salts; the range of concentration where this will occur will depend on molecular weight. Until more data are available on a wider variety of systems (especially with fractionated materials), it seems pointless to speculate further.

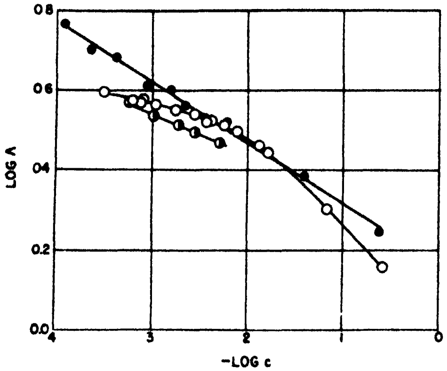

Fig. 3. Conductance curves. Solid circles, data of Reference (15); open circles, Salt 4115; half-black circles, Salt 612.

The behavior at the higher concentrations gives some information regarding local hydrodynamics in these solutions. The macroscopic viscosity of the most concentrated solution was nearly ten times that of the solvent, while that at one sixteenth the concentration was less than double. (Cf. Table III.) Still, no corresponding sharp drop in conductance occurs in this range of concentration. We can only interpret this to mean that the ions find a different (lower) resistance to their motion from that which we measure with a capillary viscometer. The situation recalls the old observation (23) that the conductance of potassium chloride in gelatin solution does not undergo a sharp change when the solution sets to a gel.

If we neglect the electrostatic effects of interionic forces, we may obtain an upper estimate for the "degree of dissociation" of the polyelectrolyte by classical methods. If the electrolyte were completely dissociated, we would have $\pi/w = 25273/m \approx 100$ and on our assumption then, the value of π/w is approximately equal to 100γ, the degree of dissociation. Using Walden's rule, we estimate the equivalent conductance Λ' of the bromide ion in our ethanol to be 53. The product $\gamma\Lambda'$ then gives the contribution of the bromide ion to the total conductance, and we are thus able to estimate the transference number of the bromide ions in the polyelectrolyte. Subtracting this quantity from unity, we obtain a value for the transference number

N+ of the polycation. The results of this calculation are given in Table V. The agreement with the γ values calculated on the basis of an entirely different set of assumptions (15) (except the neglect of interionic forces) is surprisingly good. This consistency must, of course, be due to compensation of errors because the neglected interionic terms are quite large at a dielectric constant of 30, even at ion concentrations of the order of 2×10^{-4}, the highest estimated in Table V. Comparing relative values, however, it is interesting to note that the calculated transference number is higher for the polysalt of higher degree of polymerization; since friction coefficient increases less rapidly than DP, we would expect mobility to be higher for the same degree of dissociation for the polyion of higher molecular weight.

TABLE V. Transference Numbers of Polycations

10^3c	$\pi_0/100w$	$\gamma\Lambda'$	N^+
		Salt 612	
0.563	0.049	2.60	0.30
1.027	0.047	2.49	0.27
1.854	0.046	2.44	0.25
2.751	0.042	2.22	0.29
5.046	0.040	2.12	0.27
		Salt 4115	
0.621	0.038	2.02	0.46
0.769	0.036	1.91	0.49
1.062	0.036	1.91	0.48
1.721	0.031	1.64	0.54
2.745	0.030_5	1.62	0.53
4.165	0.029	1.54	0.54
5.660	0.027	1.43	0.56
7.827	0.027_5	1 46	0.53

The addition of polyelectrolyte to lithium bromide solutions results in a decrease of conductance, as shown in Table IV. This result can be accounted for on the basis of the observed osmotic pressures in the mixed electrolytes. There we found less than an average of one free bromine ion per polyion; due to the high concentration of charge in the polyion, it could hold more than a stoichiometric equivalent of bromide ions and the unpaired lithium ions would then contribute to osmotic pressure. This extra immobilization of bromide ions would then result in a decrease of conductance. A similiar result has been observed in the case of gelation: Rettig (24) found that the conductance of gelation-salt mixtures was less than the conductance of the salt solution when salt was in excess.

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Synopsis

The osmotic pressures of two samples of poly-4-vinyl-N-n-butylpyridonium bromide (average D. P. 730 and 1900) were measured in 93% ethanol in the concentration range 0.02-0.20 g./100 cc. The osmotic pressures were higher than those of the corresponding parent polymers, due to partial dissociation of bromide ions. Because of the low dielectric constant ($\epsilon' = 28$) of the solvent and the high concentration of positive charge in the polycations, however, a large fraction of the bromide ions ($\geqslant 95\%$) were bound by electrostatic attraction to the cations and contributed neither to osmotic pressure nor to conductance. Unlike neutral polymers, the ratio (osmotic pressure over concentration) increases with dilution, due to increasing dissociation with dilution. Addition of an excess of a simple one-one electrolyte (lithium bromide) almost completely suppressed the dissociation of the polysalt and gave osmotic pressures of the same

order of magnitude as those of the neutral polymers. The resulting curves were linear, with a considerably smaller slope than for the parent polymer. Combining the results on osmotic pressure with conductance data, the transference numbers of the polycations were estimated to be 0.28 and 0.52 for degrees of polymerization 730 and 1900 respectively. The conductance of lithium bromide is decreased by the addition of these polyelectrolytes, possible due to the association of an excess of anions to the polycations under the influence of their electrostatic fields.

Résumé

Les pressions osmotiques de deux échantillons de bromure de poly-4-vinyl-N-n-butylpyridonium (D.P. moyen: 730 et 1900) ont été mesurées en solution dans l'alcool éthylique 93% à ces concentrations variant de 0.02 à 0.2 gr. dans 100 cc. Les pressions osmotiques sont plus élevées que celles des polymères correspondants, dont ils dérivent, à cause de la dissociation partielle des ions bromures. À cause de la faible constante diélectrique du solvant ($\epsilon' = 28$), et à cause de l'accumulation de charges positives dans les polycations, une grande partie des ions bromures ($\geqslant$95%) restent toutefois attachés par attraction électrostatique aux cations, et ne contribuent donc ni à la pression osmotique ni à la conductivité. Contrairement aux polymères neutres, le rapport (pression osmotique/concentration) s'accroît avec la dilution, par suite d'une dissociation progressive par dilution. Par addition d'un excès d'un électrolyte simple univalent (bromure de lithium) on peut supprimer pratiquement de façon complète cette dissociation du polyélectrolyte, et la pression osmotique l'on obtient, est du même ordre de grandeur que celle du polymère neutre. Les courbes résultantes sont linéaires; la tangente à cette droite est notablement plus faible que celle pour le polymère, dont le polyélectrolyte dérive. En combinant les résultats de pression osmotique avec ceux de la conductivité, on trouve des nombres de transport pour les polycations, égaux à 0.28 et 0.52 pour les degrés de polymérisation 730 et 1900 respectivement. La conductivité du bromure de lithium est diminuée par addition de ces polyélectrolytes, peut-être par suite d'une association d'un excès d'anions ver les polycations, sous l'influence du leurs champs électrostatiques.

Zusammenfassung

Die osmotischen Drucke von zwei Proben von Poly-4-Vinyl-N-n-Butylpyridoniumbromid (durchschnittlicher Polymerisationsgrad 730 und 1900) wurden in 93%igem Ethylalkohol in dem Konzentrationsbereich 0.02-0.20 g./100 $cm.^3$ gemessen. Die osmotischen Drucke waren hoeher als die der entsprechenden Ausgangspolymerisate wegen teilweiser Dissoziation der Bromid-Ionen. Wegen der niedrigen dielektrischen Konstante ($\epsilon' = 28$) des Loesemittels und der höhen Konzentration der positiven Ladung in den Polykationen, war ein Grossteil der Bromid-Ionen ($\geqslant$95%) durch elektrische Anziehungskraefte an die Kationen gebunden und trug infolgedessen weder zum osmotischen Druck noch zur Leitfaehigkeit bei. Im Gegensatz zu neutralen Polymerisaten steigt das Verhaeltnis des osmotischen

Druckes sur Konzentration mit Verduennung, wegen der steigenden Dissoziation, an. Zugabe eines Ueberschusses einfacher ein-einwertiger Elektrolyte (Lithium-Bromid) unterdrueckte fast gaenzlich die Dissoziation des polymerischen Salzes und ergab osmotische Drucke derselben Groessenordnung wie die neutralen Polymerisate. Die auf diese Weise erhaltenen Kurven waren linear und betraechtlich flacher als die des Ausgangspolymerisates. Auf Grund der osmotischen Druck- und Leitfaehigkeitsdaten wurden die Uebertragungszahlen der Polykationen auf 0.28 und 0.52 geschaetzt, fuer Polymerisationsgrade von 730 und 1900. Die Leitfaehigkeit von Lithium-Bromid wird durch Zugabe dieser Polyelektrolyte verringert, moeglicherweise wegen der Assoziation des Ueberschusses von Anionen unter dem Einfluss des elektrostatischen Feldes der Polykationen.

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Compléments à l'Étude de la Statistique des Chaînes Moléculaires en Solution Diluée

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INTRODUCTION

Considérons une chaîne moléculaire qui, pour la simplicité de l'exposé, sera constituée par suite d'atomes de carbone liés entre eux par des liaisons simples (1).

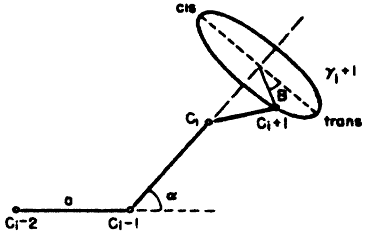

Figure 1

Nous avons représenté sur la figure 1 les positions des centres de quatre atomes successifs de la chaîne: si les points C_{i-1}, C_i, C_{i+1} sont choisis dans le plan de la figure, le point C_{i+1} peut prendre, par suite de l'agitation thermique des positions différentes situées sur le cercle Γ_{i+1}, base du cône dont le demiangle au sommet α est égal au supplément de l'angle de valence. Dans le cas d'une chaîne aliphatique $\alpha = 70°29$, $\cos \alpha = \mu = 1/3$ et l'intervalle entre deux atomes successifs C_i et C_{i+1}, appelé longueur du chaînon, est constant et égal à:

$$a = 1.54 \text{ A}.$$

Nous repérons les positions de C_{i+2} sur le cercle par les valeurs correspondantes de l'angle B que font entre eux les plans de la figure et le plan defini par C_{i-1}, C_{i+1}, C_{i+1}.

Par suite de l'agitation thermique une chaîne moléculaire comprenant N chaînons prend des configurations diverses et l'un des problemes fondamentaux est de déterminer l'écart quadratique moyen δ^2 entre les extrémités C_0 et C_N de la chaîne.

Il est clair que la valeur de δ^2 dépend de a, de α et de la loi de répartition statistique de chaque centre tel que C_{i+1} sur le cercle de base du cône de valence.

Le cas le plus simple est celui où toutes les positions sont possibles et également probables, c.à.d. celui des rotations dites "libres." Il a été examiné par Guth et Mark (2) et par W. Kuhn (3), qui ont établi à partir d'un résultat de Eyring (4) que:

$$\delta^2 = Na^2 \frac{1+\mu}{1-\mu} \qquad (1)$$

où $\mu = \cos \alpha$ dans le cas où N est très grand devant l'unité.

Dans le cas général l'expression complète donnée par Eyring (4) et aussi par Delange (5) est la suivante:

$$\delta^2 = a^2 \frac{N(1-\mu^2) - 2\mu + 2\mu^{N+1}}{(1-\mu)^2} \qquad (2)$$

Dans les cas des chaînes carbonées où $\mu = 1/3$ les valeurs de δ^2 calculées par l'expression 1 donnent un résultat qui diffère par excès de moins de 10% de la valeur calculée par l'expression 2 quand N devient supérieur à 10. L'équation 1 représente donc ainsi, dans le cas des rotations libres, une approximation largement suffisante.

Mais l'étude des vapeurs d'hydrocarbures de faible masse moléculaire montre qu'en général toutes les positions de l'atome de carbone sur le cercle de base du cône de valence ne sont pas également probables et il doit en être de même dans le cas des solutions.

En général à chaque valeur de B correspondra une énergie interne W différent. Si, par exemple, on suppose que dans la solution, la position "trans" correspond à un minimum de W, cette position sera favorisée parmi toutes les autres et il s'en suivra que l'écart δ^2 sera plus grand que dans le cas des rotations libres.

Nous nous proposons de donner ci dessous une brève analyse des résultats obtenus.

Nous remarquerons d'abord que, dans le cas des rotations libres les valeurs moyennes:

$$\eta = \cos B$$

$$\varepsilon = \sin B$$

pour toutes les positions de C_{i+1} sont nécessairement nulles. Il n'en est plus de même dans les cas ou les rotations ne sont plus libres. Si la distribution des positions de chaque point C_{i+1} sur la base du cône est symétrique par rapport au plan C_{i-1}, C_i, C_{i+1} le coefficient ϵ est nul et δ^2 dependra uniquement de a de μ et de η ; c'est le cas que nous envisagerons.

Le calcul de l'écart quadratique moyen entre les extrémités de la chaîne se divise ainsi en deux parties.

1. Exprimer la valeur de δ^2 correspondant à une valeur donnée de η .

2. Exprimer la valeur de η correspondant à une distribution de l'énergie interne W(B).

CALCUL DE δ^2 EN FONCTION DE η .

Quand η est assez petit pour que η^2 soit négligeable devant l'unité (chaîne à rotation presque libres) l'un de nous (6) avait déjà montré que l'on a:

$$\delta^2 = Na^2 \frac{1+\mu}{1-\mu}(1+2\eta) \qquad (3)$$

η étant positif ou négatif selon que la position trans ou cis est favorisée. Dans le même travail le cas opposé avait été examiné; c'est celui où la chaîne présente des configurations très voisines de la configuration tendue au maximum, c.à.d. du zig-zag planaire de longueur $L = Na\cos\frac{\alpha}{2}$ et l'on avait montré alors que:

$$\delta = L\left\{1 - \frac{2N}{3}\sin^2\frac{\alpha}{2}(1-\eta)\right\} \qquad (4)$$

Un peu plus tard Benoît (7), s'appuyant sur un travail inédit de P. Debye résolut le problème dans sa généralité et montra que, pour une valeur quelconque de η comprise entre -1 et +1 on avait:

$$\delta^2 = a^2\left\{\frac{\mu - \lambda_2}{\lambda_1 - \lambda_2} S_1 - \frac{\mu - \lambda_1}{\lambda_1 - \lambda_2} S_2\right\} \tag{5}$$

où S_1 et S_2 sont les valeurs prises par S:

$$S = \frac{N(1 - \lambda^2) - 2\lambda + 2\lambda^{N+1}}{(1 - \lambda)^2} \tag{6}$$

quand on remplace λ par λ_1 et λ_2 racines de l'équation:

$$\lambda^2 - \mu(1 - \eta)\lambda - \eta = 0 \tag{7}$$

Presque simultanément d'ailleurs H. Kuhn (8) et Taylor (9) proposaient la formule:

$$\delta^2 = Na^2 \frac{1 + \mu}{1 - \mu} \frac{1 + \eta}{1 - \eta} \tag{8}$$

valable seulement pour les valeurs de η qui ne sont pas très voisines de l'unité et dont la formule 3 représente une approximation immédiate.

Les formules 5, 6, et 7 résolvent donc entièrement le problème tandis que les formules de Sadron (pour η voisin de zéro ou de l'unité), H. Kuhn et Taylor (pour η non voisin de l'unité) représentent des approximations que l'on retrouve d'ailleurs à partir des équations 5, 6, et 7.

Nous croyons utile de montrer comment les résultats approchés donnés par l'équation 8 s'écartent des résultats exacts. Pour cela nous représenterons, pour différentes valeurs de N, les valeurs de δ/a calculées en fonction de η par les deux formules (Figs. 2 et 3).

Le domaine de validité de l'équation 8 s'étend au fur et à mesure que N augmente mais il reste évident que lorsque η tend vers l'unité, la valeur δ^2 donnée par l'équation 8 tend vers l'infini et non pas vers L^2 carré de la longueur finie du zig-zag planaire.

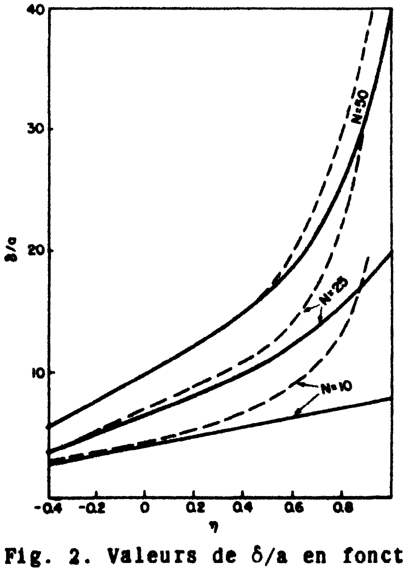

Fig. 2. Valeurs de δ/a en fonction de η pour N = 10,25, et 50; —— formule rigoureuse, --- formule approchée.

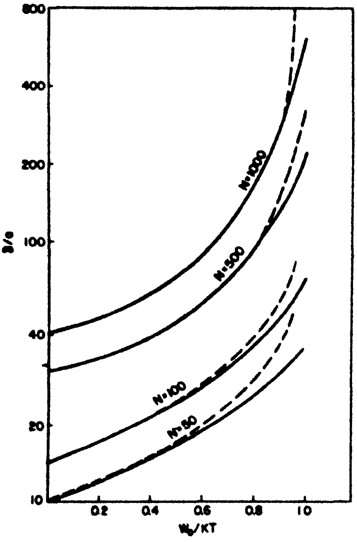

Fig. 3. Valeurs de δ/a en fonction de η pour N = 50,100, 500, et 1000; —— formule rigoureuse, --- formule approchée.

Pour illustrer cette discussion nous donnons cidessous la formule 9 qui n'est qu'une autre manière d'écrire les formules 6,7 et 8:

$$\frac{\delta^2}{a^2} = N\frac{1+\mu}{1-\mu}\,\frac{1+\eta}{1-\eta} + \frac{2}{(1-\mu)^2(1-\eta)^2}\Big\{[2\eta + \mu(1+\eta^2)](\eta D_{N-1} - 1) + [\mu^2(1-\eta) + \eta(2\mu+1) + \eta^2]D_N\Big\} \tag{9}$$

D_N et D_{N-1} étant respectivement égaux à:

$$\frac{\lambda_1^N - \lambda_2^N}{\lambda_1 - \lambda_2} \quad \text{et} \quad \frac{\lambda_1^{N-1} - \lambda_2^{N-1}}{\lambda_1 - \lambda_2}$$

Le développement de δ^2 en fonction de $1 - \eta$ est alors:

$$\frac{\delta^2}{a^2} = N^2\,\frac{1+\mu}{2}\left\{1 - (1-\mu)\left(\frac{N}{6} - \frac{3}{2N}\right)(1-\eta) + \dots\right\} \tag{10}$$

Enfin, avant d'en terminer avec ce chapitre nous remarquerons que pour des valeurs de N assez grandes l'équation 5 ou 8 se met sous la forme:

$$\delta^2 = b^2 N \tag{11}$$

avec:

$$b^2 = a^2\frac{1+\mu}{1-\mu}\,\frac{1+\eta}{1-\eta} \tag{12}$$

Pour une chaîne de Gauss nous savons que la probabilité pour que l'écart entre les extrémités soit compris entre r et r + dr est donnée par la formule:

$$P(r)dr = \frac{1}{\lambda^3}\left(\frac{3}{2\pi}\right)^{3/2} 4\pi r^2 e^{-3r^2/2\lambda^2}\,dr \tag{13}$$

avec:

$$\delta^2 = \bar{r}^2 = \int_0^\infty r^2 P(r)dr = \lambda^2$$

On pourra que, donc dès que la formule 11 est appliciable, la loi de répartition de la distance entre les extrémités de la chaîne est donnée par la formule 13 où l'on fait $\lambda = \delta^2$. On retrouve ainsi le résultat déjà donné par W. Kuhn (3) et par Guth et Mark (2) pour les chaînes à rotations libres.

CALCUL DE η À PARTIR DE LA FONCTION DE RÉPARTITION W(B) DE L'ÉNERGIE

Dans nos travaux antérieurs nous avions admis que la répartition de l'énergie présentait un minimum pour la position "trans" et que l'on pouvait en première approximation poser:

$$W = \frac{W_0}{2}(1 - \cos B) \tag{14}$$

Dans ces conditions l'un de nous a montré (1) que l'on a:

$$\eta = -i\,\frac{J_1\left(i\frac{W_0}{2KT}\right)}{J_0\left(i\frac{W_0}{2KT}\right)} \tag{15}$$

où $i = \sqrt{-1}$, K est la constante de Boltzmann, T la température absolue, J_0 et J_1 les fonctions de Bessel d'ordre 0 et 1.

Mais H. Kuhn (8) et surtout Taylor (10) ont considéré un cas plus général et sans doute plus près de la réalité en admettant que la répartition de l'énergie W en fonction de B, tout en restant symétrique, présente trois barrières de potentiel: l'une pour B = π les deux autres pour B voisin de $\pm\pi/3$. C'est ainsi que Taylor pose:

$$W(B) = \frac{W_0}{2}\left\{X(1 - \cos B) + (1 - X)(1 - \cos 3B)\right\} \qquad (16)$$

$$0 \leqslant X \leqslant 1$$

Pour X = 1 on retrouve la répartition définie par l'équation 14, fig. 4a, pour X = 0 on trouve 3 barrières de potentiel égales (fig. 4b) et pour

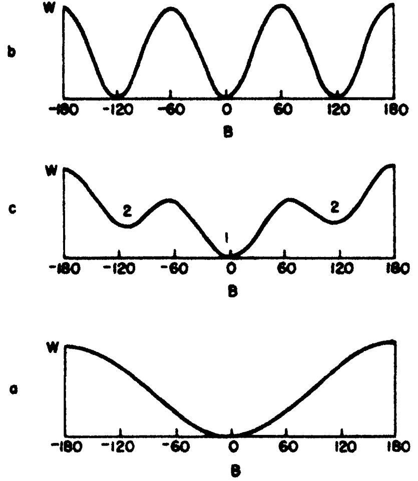

Figure 4

$0 < X < 1$ on a le cas intermediaire illustré par la figure 4c pour X = 0.5. La valeur de η dépend alors de W_0 et X et peut être calculée par la statistique de Boltzmann. La figure 5 donne les valeurs de η en fonction de W_0/KT pour X = 0.2, 0.5, 0.8, et 1. Il faut remarquer que lorsque les 3 barrières de potentiel sont égales, le coefficient η est nul quel que soit W_0/KT.

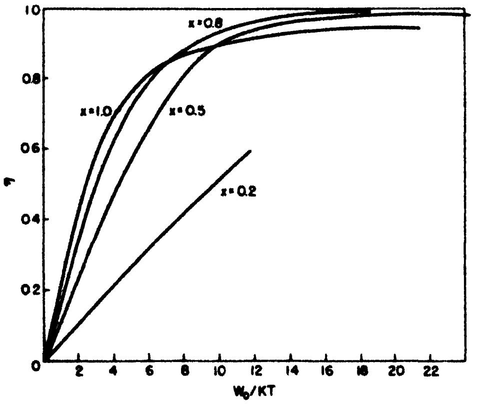

Figure 5

CALCUL DE δ^2

Connaissant ainsi les valeurs de δ^2 en fonction de η d'une part et celles de η en fonction de W_0/KT et X définissant la répartition de l'énergie, il est possible de calculer δ^2 en fonction de ces deux paramètres. C'est ce qu'ont fait Taylor et H. Kuhn de façon approchée, ainsi que nous l'avons vu. Les résultats rigoureux obtenus à partir des formules exactes, et les résultats approchés sont donnés par les figure 6 et 7 où nous avons porté les valeurs de δ/a en fonction de W_0/KT pour différentes valeurs de N dans les deux cas où X = 1 et X = 0.5.

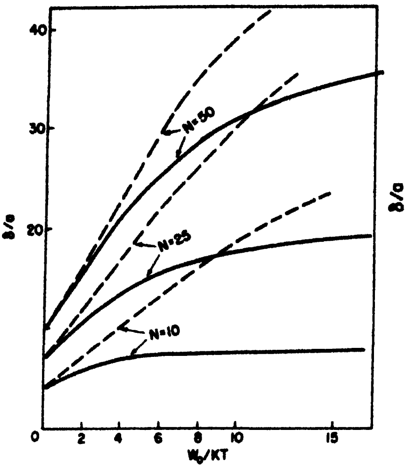

Fig. 6a. Valeurs de δ/a en fonction de W_0/KT pour N = 10,25, et 50 (X = 1); —— formule rigoureuse, --- formule approchée.

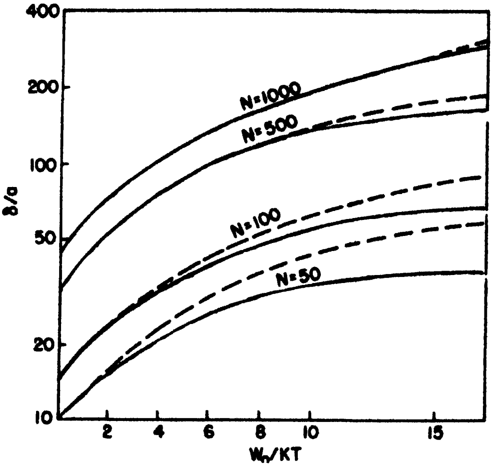

Fig. 6b. Valeurs de δ/a en fonction de W_0/KT pour N = 50,100,500, et 1000 (X = 1); —— formule rigoureuse, --- formule approchée.

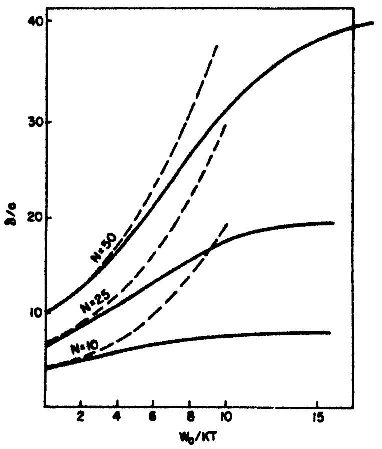

Fig. 7a. Valeurs de δ/a en fonction de W_0/KT pour N = 10,25, et 50 (X = 0.5); —— formule rigoureuse, --- formule approchée.

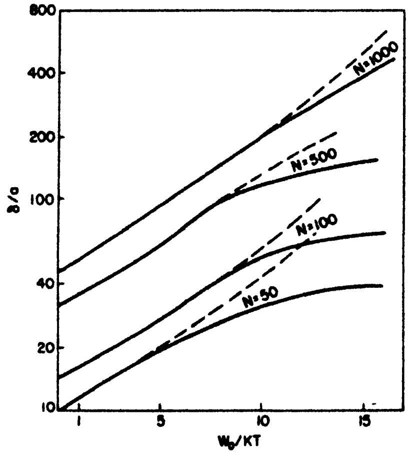

Fig. 7b. Valeurs de δ/a en fonction de W_0/KT pour N = 50,100, 500, et 1000 (X = 0.5); —— formule rigoureuse, --- formule approchée.

Ces figures permettent de déterminer facilement le domaine de validité des formules approchées. Avant d'en terminer nous désirons présenter quelques remarques sur les conséquences pratiques de la formule précédente.

1. Pour obtenir les valeurs numériques de δ^2 il est nécessaire de connaître les valeurs de W_0 et X. Taylor et H. Kuhn utilisent les

données de Pitzer (11) obtenues sur les carbures aliphatiques normaux par l'étude des spectres d'absorption infrarouge et des coefficients thermodynamiques des vapeurs. Nous ne pensons pas que cette manière de voir soit correcte car ainsi que nous l'avons signalé plusieurs fois W_0 est fonction de la nature du solvant employé et d'autant plus grand que meilleur est le solvant.

2. On peut relier la valeur de δ^2 à celle de la viscosité intrinsèque de la solution, ainsi qu'à celle de sa constante de diffusion brownienne en employant une méthode de "particule équivalente" développée par divers auteurs et en particulier par l'un de nous (12). Rappelons seulement que la méthode de la particule équivalente appliquée aux variations de la viscosité et de la constante de diffusion de translation en fonction de la température et du degré de polymérisation N permet en principe de déterminer W_0 et X.

3. Il convient de remarquer que l'on a admis implicitement jusqu'ici que le facteur W_0 est indépendant de N et de T et ne dépend que du solvant. Cette hypothèse constitue une approximation dont la validité reste à établir.

En effet le calcul de δ^2, tel qu'il a été conduit, ne fait intervenir que les interactions entre les chaînons d'ordres i et i + 2. Or ainsi qui l'ont fait remarquer de nombreux auteurs et tout récemment Simha (13) l'encombrement des atomes constituant la chaîne empêche celle-ci de prendre les configurations fortement pelotonnées qui seraient possible pour un squelette sans épaisseur.

Il s'en suit que pour la chaîne réele δ^2 doit être supérieur à la valeur calculée ci-dessus et ceci d'autant plus que η est plus petit.

On peut donc essayer de tenir compte de cet effet en ajoutant au terme W envisagé ci-dessus, un terme supplémentaire W_1 pouvant etre a priori fonction de N et de T.

De plus une deuxième raison a été signalée par l'un de nous (12): Si l'on admet que l'on puisse, en moyenne, délimiter la région de l'espace où se trouve la chaîne par une surface fermée (fig. 8) on peut distinguer l'extérieur, constitué par du solvant pur et l'intérieur, constitué par une solution des N chaînons de la chaîne. Comme la surface fermée joue approximativement le rôle d'une surface limite entre la solution et le solvant il doit s'exercer sur cette surface des tensions dirigées de l'intérieur vers l'extérieur. En effet, on peut ad-

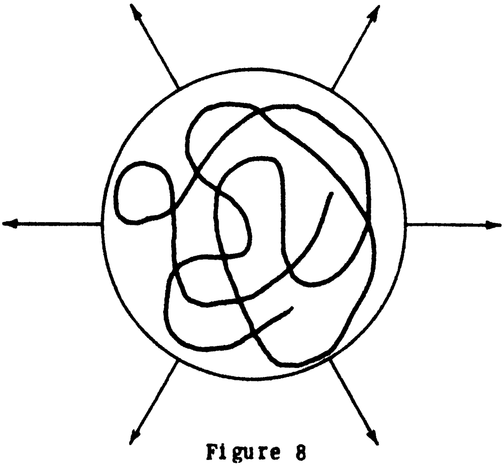

Figure 8

mettre que les chaînons qui se trouvent à la surface limite sont soumis en moyenne à une attraction provenant de l'extérieur (solvant pur) supérieure à celle qui provient de l'intérieur, (solvant contenant les chaînons). À cette tension supplémentaire devra donc correspondre un terme supplémentaire à ajouter à W_0 et W_1. Ce terme dépend de N et de T.

4. Enfin nous désirons attirer l'attention sur certaines conséquences de ce qui précède relativement à la précipitation des chaînes à partir de leurs solutions.

Cette précipitation peut être accomplie par deux procédés différents: abaissement de la température de la solution où adjonction d'une précipitant.

Il est clair que ces deux procédés ne sont pas équivalents et conduisent à des résultats différents. Supposons en effet que nous abaissons considérablement la température d'une solution très étendue.

Admettons tout d'abord que W(B) soit du type simple donné par l'équation 14. L'effet du refroidissement sera d'augmenter W_0/KT, donc de tendre chaque chaîne en zig-zag planaire. Si cet effet est obtenu au moment de la précipitation, les particules du précipité seront vraisemblablement constituées par la juxtaposition de ces zig-zag planaires en couches parallèles. Elles présenteront ainsi l'aspect d'un petit cristal fortement anisotrope. Admettons maintenant qu'il existe des barrières de potentiel du type de la figure 5c. Lorsque la température est suffisamment basse l'agitation thermique est insuffisante pour que les barrières de potentiel puissent être franchies et dans ce cas la forme limite de la chaîne n'est plus un zig-zag planaire. La configuration de la chaîne est obtenue en supposant que l'on ait n_1 atomes C_1 dans les creux 1 (fig. 4c), et $2n_2$ dans les creux 2. En supposant que tous les creux 1 se trouvent à un bout de la chaîne et tous les creux 2 à l'autre bout on obtient: $\delta^2 = 0.66a^2(n_1^2 + 2n_2)$ En supposant au contraire que la répartition est régulière on obtient la formule approchée:

$$\delta^2 = a^2 \frac{7}{27} \frac{n_1^2}{n_2}$$

avec $\mu = 1/3$.

Il est vraisemblable que la valeur correspondant à une répartition au hasard est comprise entre ces deux valeurs. Et en appliquant la statistique de Boltzmann et les résultats déjà cités de Taylor:

$$\frac{n_1}{n_2} = \exp \frac{W_0}{2} \left\{ 1 - \frac{1}{3} \frac{(3 - 4X)^{3/2}}{(3 - 3X)^{1/2}} \right\}$$

Dans ce cas il se peut que les particules du précipité présentent un aspect cristallin moins net que si la chaîne se tend en zig-zag planaire (X = 1).

Supposons maintenant que nous ajoutions un précipitant dans la solution maintenue à température constante. L'effet de l'opération est de diminuer W_0, c'est à dire de faciliter l'agitation thermique jusqu'à ce que les rotations soient pratiquement libres. Si cet effet est obtenu au moment de la précipitation celle-ci ne fournit plus de particules cristallisées mais un floculat ayant l'aspect d'un gel.

Auf dieser Grundlage wurde die Zahlenverteilung, und von ihr abgeleitet, die Gewichtsverteilung der Probe festegestellt. In der hier angefuehrten Beispielen sind die numerischen Annaehrungsoperationen so zeitraubend, dass ihre allgemeine und unmittelbare Anwendung in Frage gestellt ist. Die Schwierigkeit ist aber nicht unbedingt der Methode eigen und ist in der hier gegebenen Ausforschung ohne Belang.

Ein wichtiger Verteil einer Theorie dieser Art koennte darin bestehen, dass durch die Verbesserung der arithmetischen Analyse der Fraktionierungsgrad verringert werden koennte, wodurch die den Berechnungen angewandte Arbeit gerechtfertigt wuerde. So zum Beispiel, ist eines der schwierigeren Probleme der konventionellen Berechnungsmethode, wenn Punkte der kummulativen Gewichtsfunktion gedeutet werden, den oberen Bereich der Probe zu analysieren. Diese Schwierigkeit kann bis zu einem gewissen Grade durch die Herstellung einiger sehr kleinen Fraktionen in diesem Bereiche ueberwunden werden. Bei Anwendung der vorgeschlagenen Methode verschwindet die Notwendigkeit einer feinen Fraktionierung in diesem Bereich. Bei einem kuenstlichen Versuch und einer Reihe wirklicher Daten koennen Ergebnisse, die von den gewoehnlich gefundenen sehr verschiedensind, existieren. Der kuenstliche Versuch bestand darin, dass am Anfang angenommen wurde, dass alle Umstaende in Bezug auf einen Stoff wie Cellulose und ihre einmalige Fraktionierung bekannt sind. Bei Anwendung des Zahlendurchschnittes und des Gewichtes als einziger Daten wurde dann die Verteilung der Probe mit einzigartiger Praezision rekonstruiert. Auf der anderen Seite schien es, dass die allgemein benuetzte numerische Analyse zu Schluessen fuehrt, die weit von den anfangs angenommenen abweichen wuerden. Eine aehnliche Rekonstruktion wurde mit einer Reihe physikalischer Bestimmungen durchgefuehrt die in der Teilung einer Probe von entarteter Baumwollcellulose in fuenf Fraktionen bestand. Der Unterschied zwischen den Resultaten des auf Grund der binominalen Annahme, und dem, des durch die gewoehnliche Methode erhalten wurde, hatte den gleichen Charakter wie in den kuenstlichen Versuchen.

Es ist sehr wahrscheinlich, dass die gewoehnliche numerische Analyse von Fraktionierungsdaten irrefuehrend sein kann. Besonders leicht wird sie zu Unterschaetzungen der Menge hochpolymerer Fraktionen in der Probe fuehren.

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Light Transmission and the Formation and Decay of Spherulites in Polythene

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Although some crystalline polymers are transparent, others are opaque or translucent below the melting point, and only become clear on heating to a temperature close to that at which x-ray diffraction or volume and thermal measurements indicate a change to an amorphous structure. It is generally considered that in crystalline polymers the regions of ordered arrangement of sections of the long molecules, the crystallites, have linear dimensions of the order only of 100 A. It is thought that in the partially crystalline state the light scattering is not a direct consequence of the presence of the crystallites, but is mainly due to the presence of more or less oriented aggregates of crystallites, of dimensions greater than the wave length of visible light.

In the case of polythene, one type of oriented aggregate, the spherulite, has been described by Bunn and Alcock (1) and by Bryant (2). Spherulites are readily observed with a polarizing microscope in thin films of polythene or in polythene powder precipitated from solution. The size is variable but a typical spherulite has a diameter of the order of 1/10 - 1/100 mm. The long axes of the molecules tend to be perpendicular rather than parallel to the radii of the spherulites, although the perfection of orientation is, in general, not great. In other samples of polythene the scintillation when polarizer and analyzer are rotated indicates an oriented structure, but no individual spherulites can be distinguished.

In this paper the phenomena associated with the growth of spherulites on cooling molten polythene and their decay on raising the temperature are described, together with the associated changes in the light transmission of the sample.

LIGHT TRANSMISSION OF POLYTHENE

(a) Effect of Temperature

The changes with increase or decrease in temperature in the light transmitted through polythene film were measured in a simple semi-quantitative apparatus. A thermocouple junction was molded into a polythene sheet, 1 mm. in thickness, in a steam-heated press. The sheet was held in a horizontal position in a vessel with a plane glass base. The vessel was filled with glycerol and was fitted with a small heating coil and a stirrer. Appropriate screening was obtained by the use of an internally blackened box divided into 3 compartments containing a constant source of light, the sample, and a Weston photocell, arranged vertically one above the other. A lens was used to condense the incident light and a second lens focused the transmitted beam onto the photocell which was connected to a microammeter.

The temperature of the polythene sample was raised slowly (about 2 degrees per minute) by hand control of a resistance in the heating coil circuit, and simultaneous readings of the photocell microammeter and the thermocouple millivoltmeter were taken. Experiments with falling temperature were carried out at the natural rate of cooling of the glycerol bath (about 2°C. min.) when the heater was switched off. The current developed by the cell when the polythene was solid expressed as a percentage of the current developed when it was molten was recorded as a measure of the light transmission of the polythene specimen. It is appreciated that this apparatus measures a somewhat arbitrary combination of light absorption and light scattering and that a quantitative study would necessitate the measurement of the polar distribution of the scattered light. The apparatus is adequate, however, to give a semi-quantitative measure of what would normally be called the "transparency" of a sheet of polymer.

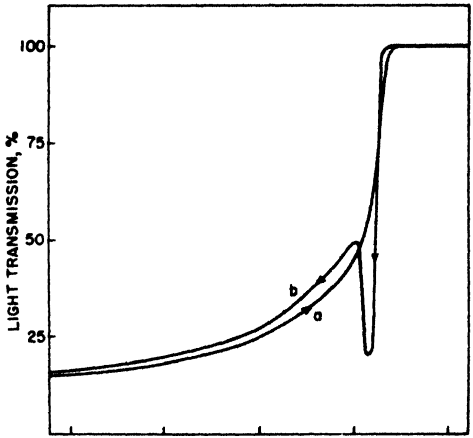

Fig. 1. Light transmission of polythene sheet as function of (a) rising and (b) falling temperatures.

Figure 1 shows the light transmission of a sample of polythene ("Alkathene 20") as a function of temperature, (a) on raising the temperature from 20°C. up to 120°C., that is, to above the melting point, and (b) on cooling again to 20°C. On raising the temperature it is seen that the light transmission increases at a steadily increasing rate up to the melting point, and thereafter remains almost constant. The change in the light transmission with increasing temperature is similar to the change in the proportion of amorphous material in the solid, as indicated by volume (3) or heat capacity (4) measurements.

On cooling from the melt a similar plot of light transmission against temperature is obtained below about 90°C. but over a range of a few degrees below the temperature at which transmission first starts to decrease (the freezing point; about 110°C.) the polymer passes through a state in which the light transmission is very low and in some samples is even less than it is at ordinary temperatures. This lack of complete similarity in the light transmission-temperature relation for rising and falling temperature led to the study under the microscope of the changes with temperature in the structure of solid polythene, which forms the second part of this paper. Before this is described, however, some of the factors affecting the variability from sample to sample of the transparency of polythene will be discussed.

(b) Variability in Transparency at Ordinary Temperatures

Using the apparatus described above at room temperature, supplemented by simple visual observation, the relative transparencies of a large number of polythene specimens have been observed. There are clearly a number of factors involved and not all are understood, but the following points have been established.

(1) There is a general tendency for the more crystalline samples, e.g., those in which the molecules are less branched, to be more opaque. This is not unexpected in view of the similarity noted above between the shapes of the amorphous content-temperature curve and the light transmission-temperature curve for rising temperature.

(2) For a given polymer sample, rapid cooling from the melt, which yields a more amorphous sample, yields also a more transparent sample. Subsequent annealing at 100°C. which increases crystallinity also increases light absorption.

(3) Absorption by the polythene of a liquid such as benzene or hydrocarbon oil increases transparency, whereas incorporation of a crystalline paraffin, for example, paraffin wax, decrease the transparency.

(4) Of a number of samples of the same degree of crystallinity as indicated by density or x-ray measurements, there is a tendency for the higher molecular weight samples to be more transparent. This generalization cannot be extended, however, to very low molecular weight materials, such as paraffin wax, or pure solid paraffins, such as hexatriacontane, which are composed of quite large separate crystals. It is of interest to note that when the crystal size of such materials is reduced by the incorporation of say 1% of polythene, the resulting products, still almost 100% crystalline, are now much more opaque than normal polythenes which are 70-80% crystalline.

GROWTH AND DECAY OF SPHERULITES IN POLYTHENE

The spherulitic structure typical of polythene can conveniently be observed in a film of thickness of about 0.1 mm. resting on a glass slide under a polarizing microscope. Such a film may consist only of one layer of spherulites and these may therefore be recognized as dark crosses on a light ground (when the Nicols are crossed) which appear to rotate as the polarizer and analyzer are rotated together. In order to observe and record the effects of rising and falling temperature on the structure of the film, a platinum wire (40 gage), which could be heated by a 6-volt battery with a controlling resistance, was embedded in the polythene. The microscope was fitted with a prism which diverted about one-tenth of the transmitted light through a right-angle to the eyepiece, transmitting the remainder either to a 2 1/4 x 3 1/4 inch camera or to a 16 mm. ciné camera. It was thus possible to observe and to photograph the changes in the film at the same time.

(a) Changes on Raising the Temperature to the Melting Point

Plate II[1] illustrates the changes in structure as the temperature is raised. (This is a photomicrograph taken with crossed Nicols). The wire is to the right of the field and is being heated in an initially cold polythene film. All parts of the field are thus rising in temperature but there is a temperature gradient falling from right to left. The left-hand edge of the field shows the spherulitic structure of the cold solid, the right-hand edge adjacent to the wire shows the structureless molten polymer, while in the middle the spherulites are seen to become less well defined but to have the same general outline.

(b) Changes on Cooling from the Molten State

These are observed by heating the wire until the whole field is clear and then reducing the current. In the photographs the left-hand edge of the field furthest from the wire has cooled more than the right-hand edge.

The first type of structure formed from a clear molten polymer is seen as a uniformly mottled background, in which light is scattered and in which there is some form of orientation. This type of structure is not observed when the polymer is being heated. The next effect is the formation of apparently randomly spaced nuclei in this phase, and from them spherulites grow rapidly, appearing as circles expanding at a constant linear rate until they meet other spherulites. The spherulite nuclei do not all appear at the same time. Those which start growth later are the smaller ones in the final film.

These changes are illustrated in Plates III and IV. Plate III is a series of five extracts from a ciné film showing the growth of spherulites from an initially clear field of molten polymer. In these reproductions the initial fine structure from which the spherulites grow cannot be seen, but it is seen clearly with a sharp boundary between it and the molten zone in the photomicrograph reproduced in Plate IV, which corresponds approximately to the middle extract of Plate III. In Plates III and IV the Nicols are only partially crossed. The heating wire appears as a black zone as the extreme right-hand edge of the photograph, and the molten zone is the adjacent, light-colored, zone. The spherulites appear not as crosses on a light ground, (as in Plates II and V) but as circles with two opposite quadrants dark and light).

(c) Repeated Melting and Solidification

When a film was melted, allowed to solidify, remelted until the whole field was clear, and then immediately allowed to cool again, the spherulites in the second crystallization appeared in the same places and in the same order as in the first melting, so that the final pattern was almost identical with the initial one. If, however, the film was held in the molten state for about 5 minutes before cooling the second time, a new set of spherulites appeared. The retention for a time in the same place of nuclei for spherulite growth is, of course, favored in this experiment by the high viscosity of the polymer and by the thinness of the film. It is possible that the nuclei are actually on the surface of the microscope slides.

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[1] The Plates referred to in this paper are at the end of this issue.

(d) Solidification after Partial Melting

When the temperature was reduced after the sample had been heated to a temperature which was only adequate to melt about half of the field, it was found that although the normal spherulites were formed in the zone close to the wire, a band of very small oriented regions (possibly small spherulites; each only about 1/100th of the area of the original spherulites) was formed in the section of the film immediately to the high temperature side of the frontier between partially molten spherulites and the apparently structureless zone.

This is shown in Plate V. When this portion of film is remelted so that the whole field is featureless and is then cooled, the normal larger spherulites reappear.

DISCUSSION

The microscopic examination reported here, combined with the x-ray work of Bunn and Alcock (1), appears to give a satisfactory explanation of the light transmission results.

We consider that the lack of transparency in solid polythene is due primarily to internal reflection at the boundaries between spherulites where there is a change of refractive index. Some scattering of light may occur within the spherulites themselves; small locally oriented aggregates of the type first formed from the melt (Plate IV) may persist to certain extent after the spherulites have formed, and a fine structure inside the spherulite boundaries can be seen in certain cases. We consider, however, that it is the spherulite boundaries which are the chief cause of light scattering.

The change in refractive index at any boundary will be greater the greater the degree of orientation or crystallization within the spherulites. The transparency of the sample will hence depend on the average size of spherulites, that is, the number of spherulite boundaries through which the light has to pass, and also on the perfection of orientation in the spherulites, which in turn will be affected by the degree of crystallinity of the sample. On raising the temperature of a sample of polythene, the proportion of crystalline material decreases at an increasing rate. Bunn and Alcock's work (1) indicates that this takes place by the successive melting of crystallites in order of increasing size. The spherulite thus becomes less well defined, the perfection of radial orientation decreasing and the change in refractive index at the boundaries with adjacent spherulites being less marked. The general outline of the spherulite remains until the last and largest crystallites have melted (and possibly even at higher temperatures as a zone of imperfect radial orientation). The scattering of the light decreases continuously throughout this process. On cooling, on the other hand, the spherulites grow not directly from the melt but from a partly crystalline phase in which there is some form of orientation over small zones. It is suggested that it is this phase which corresponds to the region of very low light transmission observed when polythene is cooled a few degrees below the freezing point (curve b of Figure 1) and that the orientation of the crystallites into relatively large spherulites with a consequent reduction in the number of discontinuities in refractive index causes the subsequent temporary increase in transsparency. Further cooling causes an increase in the crystallinity and hence greater changes in refractive index at the spherulite boundaries and hence to greater light scattering.

The growth of spherulites from molten polythene through an intermediate phase with less perfect orientation is superficially very similar to the growth of spherulites from a liquid crystal phase in the case of materials such as cholesteryl acetate (5).

The formation of the zone of small oriented regions at the boundary between a partially melted and completely melted material when the temperature increase is reversed requires some explanation. It is suggested that, when an almost completely melted spherulite is cooled, the few crystallites which remain (the largest crystallites of the cold solid) act as separate nuclei for new regions of local orientation, possibly small spherulites.

Finally, the question of the size of spherulites may be discussed. As in the case of the growth of single crystals of low molecular weight material, the size is a function of the number of nuclei formed and this is affected by such things as the rate of cooling and the presence of extraneous matter, for example, dust particles or the surface of the containing vessel. The size of the spherulites in a large number of polythene samples has been observed but it has not been found possible to obtain a clear-cut correlation of the average spherulite size with other structural features. There appears to be no correlation between the degree of crystallinity and spherulite size but there is perhaps a tendency for the higher molecular weight samples to give larger spherulites and this may be the explanation of the increase in transparency as molecular weight increases, although this may also be due to decreased orientation in the spherulites as molecular weight increases.

The authors wish to acknowledge the part taken in this work by Mr. H. Emmett, who assisted with the microscopic observation and made the ciné film on which Plate III is based.

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Synopsis

The effect of increasing and decreasing temperature on the light transmission of polythene has been measured. On raising the temperature of a sheet of polymer the light transmitted increases steadily at an increasing rate until the sample becomes glass clear at the melting point (ca. 112°C.). On cooling from the melt the specimen becomes very opaque a few degrees below the melting point, then becomes much more transparent and thereafter the light transmission decreases as temperature falls, the transmission-temperature curve approximating to the curve for rising temperature. Changes in the spherulite structure of polythene film on heating and cooling have been observed under the microscope and recorded on a ciné film. Decay of spherulites on heating is seen not to occur by the reverse of the process by which they are formed from the melt, and the light transmission results are discussed in relation to the spherulitic structure of the polymer.

Résumé

L'influence d'une augmentation ou d'une diminution de température sur la transparence à la lumière du polyéthylène a été mesurée. En augmentant de la température d'une feuille de polyéthylène la transparence augmente régulièrement avec une vitesse croissante jusqu'à ce que l'échantillon devient limpide au point de fusion (ca. 112). En refroidissant de ce produit fondu, l'échantillon devient très opaque à quelques degrés en dessous du point de fusion, puis acquiert une transparence plus prononcée; ultérieurement la translucidité diminue à mesure que la température diminue et la courbe de transparence en fonction de la température se rapproche de celle obtenue en augmentant la température. Des variations de la structure sphérulitique du film de polyéthylène ont été observées au cours du chauffage et du refroidissement au moyen du microscope; elles ont été enregistrées sur film cinématographique. La disparition des spherulites par chauffage ne correspond pas au phénomène inverse de leur formation au départ du produit fondu; les résultats de transparence ont été mis en rapport avec cette structure sphérulitique de polymère.

Zusammenfassung

Die Wirkung steigender und fallender Temperatur auf die Tranzparenz des Polyaethylens wurde gemessen. Wenn eine Platte des Polymers erhitzt wird, steigt die Tranzparenz mit wachsender Schnelligkeit bis die Platte am Schmelzpunkte (112°C.) glasklar wird. Bei Kuehlung der geschmolzenen Masse truebt sich die Probe stark einige Grade unter dem Schmelzpunkt, wird dann viel durchsichtiger, wonach die Durchsichtigkeit mit fallender Temperatur proportional zur Erhitzungskurve. Veraenderungen in der Spherulitenstruktur von Polyaethylen-Filmen bei steigender und fallender Temperatur werden

mikroskopisch beobachtet und gefilmt. Kehrt man den Vorgang um und laesst die Spherulite aus der Schmelze entstehen, so findet kein Verschwinden beim Erwaermen statt. Die Transparenzergebnisse werden in Bezug auf die spherulitische Struktur des Polymers eroertert.

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LETTER TO THE EDITORS

ÉTUDE VISCOSIMÉTRIQUE DE LA STRUCTURE MOLÉCULAIRE DE LA GÉLATINE EN SOLUTION*

Dans le cadre d'une étude entreprise en vue de déterminer la structure de la gélatine, nous avons recherché l'influence du pH et de la force ionique de la solution sur la viscosité intrinsèque de cette protéine. La gélatine qui est obtenue par hydrolyse plus ou moins poussée d'un collagène renferme des fractions de masses moléculaires différentes dont les limites extrêmes sont de l'ordre de 5,000 et 400,000.

Nos mesures ont porté sur des gélatines commerciales non fractionnées et sur des échantillons homogènes obtenus à partir des gélatines commerciales ci-dessus par fractionnement, par coacervation selon la technique de Dobry (1) et dont l'application au cas de la gélatine a été décrite par l'un de nous (2).

Il est admis qu'au dessus de la température de transformation gel-sol, la gélatine est dispersée moléculairement en formant une solution vraie. Les résultats donnés ci-dessous semblent d'ailleurs confirmer cette hypothèse. Au-dessus de cette température de transformation, température qui n'est pas une constante, mais qui dépend en particulier de l'origine et des traitements subis par la gélatine, les viscosités des solutions diluées de gélatine sont indépendantes du gradient de vitesse. Autrement dit, à ces températures, les solutions de gélatine sont des liquides newtonniens.

Les gélatines étudiées furent déminéralisées par la méthode de Loeb et dissoutes dans des solutions tamponnées. Le tampon utilise est un mélange équimoléculaire d'acides acétique, phosphorique et borique additionne de la quantité de soude suffisante pour obtenir le pH désiré.

Ce mélange permet d'effectuer des mesures à tous les pH sur des solutions ayant toutes même pouvoir tampon et même force ionique.

Si pour un pH et une force ionique donnés de la solution de gélatine, on porte les viscosités réduites η_{sp}/c en fonction de la concentration c en gélatine, on obtient une droite pour des concentrations comprises entre 0.1 et 12% quels que soient le pH (entre 2.5, et 9), la force ionique et la nature de la gélatine. Sur la fig. 1 sont reportés quelques résultats obtenus avec différentes gélatines commerciales et différentes fractions homogènes en solution isoélectrique. La linéarité de la courbe η_{sp}/c en fonction de c permet de définir une viscosité intrinsèque $[\eta]$. Il est à remarquer que dans tous les cas cette droite est peu inclinée.

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*Communication No. 1254V des Laboratoires de Recherches de la Société Kodak - Pathé (France).

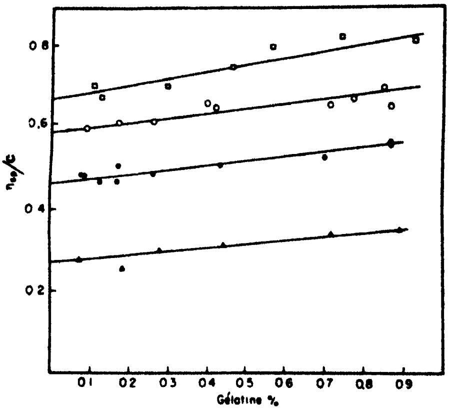

Fig. 1. η_{sp}/c en fonction de la concentration pour différents échatillons de gélatine. Le pH de chaque solution est égal au pH isoélectrique de la gélatine considérée.

Si en maintenant le pH constant, on modifie la force ionique de la solution en faisant varier la concentration en sels tampon on observe que la viscosité intrinsèque varie considérablement alors que les variations de la pente de la droite η_{sp}/c en fonction de c minimes. Les résultats obtenus avec une gélatine de peau de point isoélectrique 4.7 en solution isoélectrique sont reportés sur la fig. 2. La viscosité intrinseque croît d'abord rapidement avec la concentration saline, passe par un maximum aplati puis décroît. L'augmentation de la viscosité intrinsèque avec la force ionique s'accorde avec les hypothèses généralement formulées sur la structure de la gélatine. Au pH isoélectrique la gélatine porte des nombres égaux de groupes

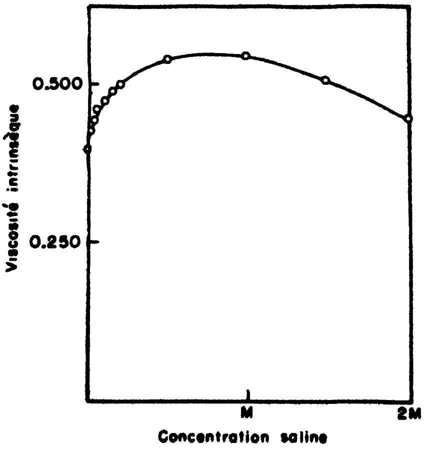

Fig. 2. Influence de la force ionique de la solution sur la viscosité intrinsèque de la gélatine.

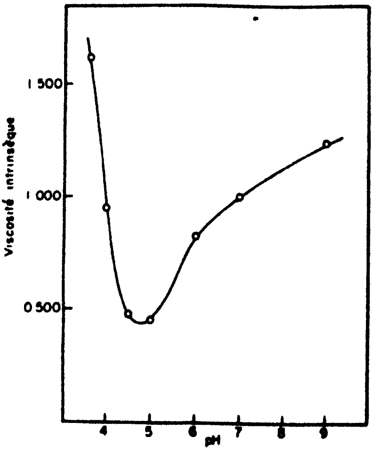

Fig. 3. Variation de la viscosité intrinsèque avec le pH. Gélatine de peau de point isoélectrique 4.7.

acides et de groupes amines ionisés et les attractions énergiques entre les différentes parties d'une même molécule tendent à pelotonner la molécule. Une augmentition de la force ionique de la solution diminue le degré d'ionisation et on peut admettre que les forces attractives entre les groupes polaires sont diminuées. Ce relachement des liaisons intramoléculaires entraîne une extension de la molécule de gélatine et, par suite, une augmentation de la viscosité intrinsèque.

Des mesures de pression osmotique ont montré d'autre part que le poids moléculaire mesuré par extrapolation à dilution infinie n'est pas influencé par la concentration saline des solutions.

Ce comportement est différent de celui observé par Fuoss et Strauss (3) sur le bromure de polyvinylbutylpyridonium et par Pals et Hermans (4) sur le pectinate de sodium. Cette différence provient sans doute du fait que contrairement au cas de la gélatine en solution isoélectrique, les groupes ionisés portés par ces hauts polymères sont tous du même signe.

Si, à force ionique constante, on fait varier le pH de la solution, il apparait que la viscosité intrinsèque est minimum au pH isoélectrique (fig. 3), ce qui est normal puisqu'à ce pH la molécule tend à se pelotonner par suite de l'exaltation des attractions intramoléculaires.

Dans un intervalle de température compris entre 31 et 45°C, on observe (fig. 4) que la viscosité intrinsèque varie peu si l'on maintient le pH et la force ionique à une valeur donnée. Ce resultat semble prouver que la gélatine en solution à ces températures est à l'état de dispersion moléculaire, car si les molécules de gélatine étaient associées, une élévation de température modifierait l'état d'association et, par conséquent, la viscosité intrinsèque.

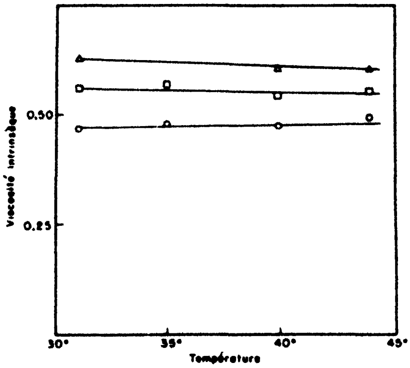

Fig. 4. Influence de la température sur la viscosité intrinsèque de solutions de gélatine. Mesures effectuées sur des solutions de pH différents: Δ, pH = 4.0; o, pH = 4.7; □, pH = 5.0.

En terminant, nous tenons à remercier M. le Docteur M. L. Huggins pour ses conseils qui nous furent si précieux au cours de cette étude.

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LETTER TO THE EDITORS

SOLUBILITY OF POLYETHYLENE IN XYLENE

In the Flory-Huggins equation for the reduced osmotic pressure of dilute polymer solutions:

$$\pi/c_2 = \frac{RT}{M_2} + Bc_2 \qquad (1)$$

B appears as the slope in the plot of π/c_2 in unit grams of force per square centimeter against polymer concentration in grams per 100 cc. of solution; it is given by:

$$B = RT/V_1 d_2^2 (1/2 - \mu) \qquad (2)$$

where V_1 and d_2 are the partial molar volume of the solvent and the density of the polymer, respectively, μ is a semi-empirical constant characteristic for the interaction of the molecules of the solvent with the segments of the macromolecules and hence offers a convenient measure for the solubility of the polymer.

In a recent paper, Doty et al. (1) showed that the solubility of polymers is highly sensitive to even small degrees of branching in the sense that an isolated branched macromolecule is characterized by a higher degree of local concentration of segments than an isolated linear molecule of the same type and the same molecular weight in the same solvent. Thus, there is more segment-segment contact in a branched molecule in solution than in a linear one and the solute-solvent interaction is decreased; this has been established by observing an increase of μ in the branched species. The μ value is essentially independent of the molecular weight and was found to be noticeably higher for a branched macromolecule than for its linear counterpart provided other configurational changes do not occur in solution. Boyer and Spencer (2) in the measurement of the swelling of a series of polystyrene-divinylbenzene gels of different compositions have observed that the value of μ varies linearly with the degree of cross-linking in macromolecules.

Osmotic pressure measurements were carried out with six polyethylene samples[1] of the same type as were previously subjected to an extensive study of Bryant (3) in the course of which he established that they possess different degrees of branching. This was concluded from different ratio of CH_2 to CH_3 groups as determined independently by infrared absorption and by the method of Kuhn and Roth. The larger the number of CH_2 to CH_3 groups the smaller is the degree of branching of the macromolecules; high numbers in the third column of Table I indicate low degree of branching.

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[1] We are very much indebted to Dr. W. M. D. Bryant of E. I. du Pont de Nemours and Co. for very kindly putting these valuable samples at our disposal.

The osmotic pressure measurements were carried out with Zimm-Meyerson glass osmometers (5) at 72.7°C. in a thermostatted bath; the measurements with the last sample were made at 91.6°C., because this material required higher temperatures and longer time to go into solutions. Though the solubility of the polymer samples decreases with increasing molecular weight, all except the last sample were completely soluble at the temperature at which the osmotic measurements were made. Precipitation occurred at about 10 degrees below the temperature of the bath.

TABLE I

Sample No.	Density[a]	Ratio CH_2 to CH_3[a]	$[\pi/c]_{c\to 0}$	Temp., °C.	$\bar{M}n \times 10^{-3}$	μ value
1	0.91	12	29.6	72.7	9.91	0.516
2	0.917	21	11.2	72.7	26.20	0.511
3	0.925	22	25.3	72.7	11.60	0.514
4	0.929	38	17.6	72.7	16.66	0.506
5	0.926	62	7.7	72.7	38.10	0.507
6	0.936	330	8.3	91.6	37.30	0.503

[a] These data were kindly supplied by Drs. W. M. D. Bryant and W. Franta of E. I. du Pont de Nemours and Company.

Table I shows the results obtained with six samples; they are arranged according to the value of CH_2/CH_3 in such a manner that the highly branched species are on the top of the table whereas the less branched samples are at the bottom. The density as given in column 2 generally increases as branching decreases (only samples 4 and 5 are in reverse order). The μ values show a general tendency to decrease as branching decreases and cover a range from 0.516 to 0.503. Samples 2 and 5 are slightly out of line, but the data indicate that the μ values of branched polythene molecules in xylene are larger than those of unbranched ones. This is in line with the observations of Doty, Brownstein, and Schlener (1) and of Boyer and Spencer (2) and seems to confirm that segment-segment contacts develop more readily between the various parts of a branched than of an unbranched macromolecule.

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LETTER TO THE EDITORS

OSMOTIC MEASUREMENTS OF ISOMERIC POLYVINYL ISOBUTYL ETHERS

Schildknecht, Zoss, and Clyde (1) have described two types of polyvinyl isobutyl ether; one is a soft, tacky, and rubberlike product, the other is crystalline and fibrous. Osmotic pressures were measured on two samples, which Dr. Schildknecht kindly provided for this investigation, in a Zimm and Meyerson (2) osmometer. The molecular weight and the μ values were calculated by the expression:

$$\pi/c_2 = \frac{RT}{M_2} + \frac{RT}{V_1 d_2^2}(1/2 - \mu)$$

where π = osmotic pressure measured in grams of force per square centimeter, R = 848, T = temperature (300.3°K.); V_1 = molar volume (107 for toluene); d_2 = specific gravity of the solute, 0.93; c_2 = concentration of solute in grams per 100 cc.; and μ = constant for the interaction of solvent molecules with segments of the polymer molecules.

Viscosities of the two polymers were determined in toluene at 27.6°C. in an Ostwald viscometer. Plots of the quotient of specific viscosity and concentration against concentration of the polymer in grams per 100 cc. of solution, gave straight line graphs from which (by extrapolation to infinite dilution) 2.95 and 3.90 were obtained as intrinsic viscosity of the soft and hard polymers, respectively.

The results are given in Table I.

TABLE I

	Soft polymer	Hard polymer
Solvent	Toluene	Toluene
Specific gravity	0.93	0.93
Molecular weight	5.54×10^5	2.12×10^5
μ value	0.455	0.481
Intrinsic viscosity $[\eta]_{c\to 0}$	2.95	3.90

The fibrous polymer needs special care to be properly dissolved in toluene, whereas the soft rubbery modification is rather easily soluble. The molecular weight of the soft polymer is about two times that of the hard one, which seems to be in line with the general experience that unmoderated ionic catalysts lead to higher molecular weights than moderated systems. The μ value as well as the intrinsic viscosity of the hard crystalline modification is noticeably larger than that of the soft and rubbery species. It appears that macromolecules of the former type favor segment-segment interaction as compared with segment-solvent contact, and, as a consequence, are difficulty soluble. In the present case the poor solubility goes parallel with easy crystallization, which makes it seem that the reason for enhanced segment-segment interaction is a more regular arrangement of the individual monomer units in the chain of the hard polymer as compared with the soft species.

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LETTER TO THE EDITORS

ULTRASONIC VELOCITY IN MACROMOLECULAR SUBSTANCES

In a recent paper (1) we reported that the ratio of ultrasonic velocity to density in molten or dissolved macromolecular substances is related to the average molecular weight and the amount of branching in the molecule.

In a successive paper (2) we introduced the shape factor as the ratio of experimentally determined ultrasonic velocity to the calculated one, using Rama Rao's law (3) and utilizing Lagemann and Corry's values (4) of the ultrasonic bond velocity.

As these data clearly show, straight-chain and unbranched molecules present shape factors equal or near to unity, while branched molecules yield shape factor values below unity.

Further work on ultrasonic velocities in some low-molecular hydrocarbons, ethers, and esters discloses that divergencies between experimental and calculated values, as observed in high molecular compounds, exist also in low molecular substances, though the numerical values of the differences were considerably smaller in the latter. Therefore, Lagemann and Corry's ultrasonic bond velocities must be corrected in order to allow predictions of ultrasonic velocities in branched compounds.

For this purpose we have found it more suitable to consider ultrasonic radical velocities rather than bond velocities, or Rama Rao's atomic velocities.

Thus we assume that the ultrasonic molecular velocity:

$$R = \frac{u^{1/3}}{\rho} M$$

(u = ultrasonic velocity, ρ = density, M = molecular weight) as the sum of all terms which correspond to each one of the radicals composing the molecule.

Form the measured ultrasonic velocities of the first liquid members of the series of hydrocarbons, ethers, and esters we have calculated the following values of ultrasonic radical velocities:

$$-CH_3 = 288 \quad -CH_2- = 192 \quad -\overset{|}{\underset{|}{C}}H = 90 \quad -\overset{|}{\underset{|}{C}}- = -10$$

$$-C_6H_5 = 870 \quad -O-(\text{ethers}) = 65 \quad -\underset{\substack{\| \\ O}}{C}-O- \ (\text{esters}) = 260$$

However we observed that lower values for radical velocities have to be used if the radicals are bound in side positions with respect

TABLE I

Substances	n_B/n_C*	Branching type	Shape factors from bond velocities	Ultrasonic molecular velocities			Differences between experimental velocities and calculated velocities	
				Experimental	Calc. from bond velocities	Calc. from radical velocities	From bond velocities	From radical velocities
n-Hexane	0	-	1.007	1357	1354	1344	+ 3	+13
n-Heptane	0	-	0.979	1538	1548	1536	-10	+ 2
2-Methylbexane	0.167	CH_3	0.970	1533	1548	1531	-15	+ 2
3-Methylhexane	0.167	CH_3	0.949	1521	1548	1519	-27	+ 2
3-Ethylpentane	0.2	C_2H_5	0.930	1513	1548	1511	-35	+ 2
2,2-Dimethylpentane	0.4	CH_3	0.957	1526	1548	1526	-22	0
2,4-Dimethylpentane	0.4	CH_3	0.956	1526	1548	1526	-22	0
2,3-Dimethylpentane	0.4	CH_3	0.930	1511	1548	1514	-37	- 3
3,3-Dimethylpentane	0.4	CH_3	0.917	1505	1548	1502	-43	+ 3
2,2,3-Trimethylbutane	0.75	CH_3	0.908	1500	1548	1509	-48	- 9
n-Octane	0	-	0.969	1725	1743	1728	-18	- 3
2,2,4-Trimethylpentane	0.6	CH_3	0.933	1706	1743	1701	-37	+ 5

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* n_B = number of branchings; n_C = number of carbon atoms in principal chain.

TABLE II

Substances [a]	n_B/n_C	Branching type	Shape factors from bond velocities	Ultrasonic molecular velocities			Differences between experimental velocities and calculated velocities	
				Experimental	Calc. from bond velocities	Calc. from radical velocities	From bond velocities	From radical velocities
Natural paraffin (m.p. 60°)		-	1.00	195	194	192	+ 1	+ 3
Fischer paraffin (m.p. 90°)	-	-	1.02	196	194	192	+ 2	+ 4
Polyethylene ($\eta_{sp}/c=8$; $c=0.1/0.$[illegible])	0	-	1.01	195	194	192	+ 1	+ 3
Polyethylene oxide ($\eta_{sp}/c=7$; $c=0.1/0.$[illegible])	0	-	1.03	458	454	449	+ 4	+ 9
Nylon 6.6	0	-	1.00	2500	2500	2504	0	- 4
Polyisobutylene ($\eta_{sp}/c=1$; $c=1$)	1	CH_3	0.79	718	778	734	-60	-16
Polyisobutylene ($\eta_{sp}/c=2$; $c=1$)	1	CH_3	0.79	719	778	734	-59	-15
Polyisobutylene ($\eta_{sp}/c=3.5$; $c=1$)	1	CH_3	0.79	717	778	734	-61	-17

TABLE II *(continued)*

Substances[a]	n_B/n_C	Branching type	Shape factors from bond velocities	Ultrasonic molecular velocities			Differences between experimental velocities and calculated velocities	
				Experimental	Calc. from bond velocities	Calc. from radical velocities	From bond velocities	From radical velocities
Polyisobutylene (η_{sp}/c=250; c=0.1/0.3)	1	CH_3	0.80	722	778	734	-56	-12
Polyalphabutylene (η_{sp}/c=1.2; c=1)	0.5	C_2H_5	0.82	729	778	742	-49	-13
Hydrogenated Buna 32 (η_{sp}/c=0.5; c=1/5	1 or 0.5	CH_3 or C_2H_5	0.82	729	778	734 or 742	-49	~ -10
Butyl rubber (η_{sp}/c=15; c=0.1/0.5)	?	?	0.65	674	778	-	-105	-
Polystyrene (η_{sp}/c=14; c= 0.1/0.5)	0.5	C_6H_5	0.82	1090	1165	1152	-75	-62
Polyvinyl isobutyl ether (η_{sp}/c=50; c=0.1/0.3)	0.5	$O\text{-}CH_3\text{-}\overset{CH_3}{\underset{CH_3}{CH}}$	0.78	1138	1232	1180	-102	-42
Polymethyl methacrylate (η_{sp}/c=15; c=0.1/0.3)	1	$\begin{cases} CH_3 \\ OOCCH_3 \end{cases}$	0.63	887	1033	998	-146	-111

---

[a] m.p. = melting point; η_{sp} = specific viscosity; c = base moles in 1000 cc. of solvent.

to the main chain of the molecule. This lowering has been calculated to be -12 for $-CH_3$ radicals and -20 for $-C_2H_5$ radicals.

In Table I are reported data relating to ultrasonic velocities of low molecular hydrocarbons; the molecular velocities have been calculated introducing the lowering correction for $-CH_3$ and $-C_2H_5$ branching. The table shows that if radical velocities are applied calculated ultrasonic molecular velocities and experimental ones are in better agreement than if bond velocities are applied.

Even for high molecular substances, reported in Table II, the differences between calculated ultrasonic molecular velocities and experimental ones are smaller if radical velocities are applied instead of bond velocities. However, these differences are still considerable, especially for the last substances in this table.

Since in the calculation of the molecular velocities we have only considered the branching-lowering correction for the $-CH_3$ and $-C_2H_5$ radicals, the differences between the experimental and calculated values have to be ascribed to the branching-lowering due to $-\underset{\underset{O}{\|}}{C}-O-$, $-O-CH_2-\underset{|}{\overset{|}{C}}H$ and $-C_6H_5$ radicals.

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Centro di studio per la Chimica Industriale del C. N. R.
presso il Politecnico di Milano, Italy

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ERRATA

Errata: SPECIFIC REFRACTIVITY-TEMPERATURE DATA FOR POLYVINYL ACETATE AND POLYBUTYL ACRYLATE

(J. Polymer Sci., 4, 351-357, 1949)

by Richard H. Wiley and G. M. Brauer
Venable Chemical Laboratories, University of North Carolina

Page 352, insert the following between lines 25 and 26:

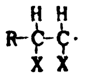
sphere was derived by assuming that the forces by the atom inside this

Journal of Polymer Science Vol. IV, pp. 539-541, 1949

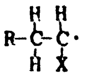
LETTER TO THE EDITORS

ACID-CATALYZED COPOLYMERIZATION BEHAVIOR OF ANETHOLE

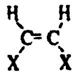
It has been repeatedly observed that 1,2 disubstituted ethylenes exhibit a specific reluctance to add to themselves in free radical copolymerization reactions (1). This has been recognized as a steric effect. A highly substituted free radical, of the form (a) below, has difficulty in adding to the double bond of a highly substituted olefin such as (c), although reactions such as (a) + (d), or (b) + (c), below (in which either the monomer or the radical is less highly substituted) can occur with ease.


$\mathrm{R{-}\underset{X}{\overset{H}{C}}{-}\underset{X}{\overset{H}{C}}\cdot}$

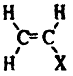
(a)


$\mathrm{R{-}\underset{H}{\overset{H}{C}}{-}\underset{X}{\overset{H}{C}}\cdot}$

(b)



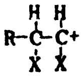
(c)



(d)

We do not imply that the reaction between a free radical such as (a) and an olefin such as (c) is completely prohibited. Doak (2) has reported that, in the free radical copolymerization of vinylidene chloride with diethyl fumarate, diethyl fumarate adds to itself at an appreciable rate. However, in most cases involving a 1,2 disubstituted monomer, the reactivity ratio product r_1r_2 is extremely small and, further, 1,2 disubstituted olefins show, at best, only a very small tendency to polymerize alone by a free radical mechanism.

The fact that 1,2 disubstituted ethylenes have often been observed to polymerize by the "acid-catalyzed" mechanism leads to the tentative conclusion that a highly substituted carbonium ion is not markedly retarded by steric effects from adding to a 1,2 disubstituted double bond. One crucial experiment on this point is the copolymerization by carbonium ion mechanism of a vinyl-type monomer with a 1,2 disubstituted monomer. If copolymers containing over 50% of the 1,2 disubstituted monomer can be obtained, this indicates that the substituted monomer (c) can compete favorably with the less substituted monomer (d) for a carbonium ion of the structure (e).


$\mathrm{R{-}\underset{X}{\overset{H}{C}}{-}\underset{X}{\overset{H}{C}}^{+}}$

(e)

It was decided to obtain and compare the copolymer composition curves for the peroxide and acid-catalyzed copolymerizations of anethole (p-methoxy-β-methylstyrene) and o-chlorostyrene.

Acid catalysis gave copolymers much richer in anethole than the corresponding monomer mixtures at all concentrations. Peroxide catalysis gave copolymers much poorer in anethole, the composition curve being consistent with the value $r_2 = 0$. The results are summarized in Tables I and II.

TABLE I. Free-Radical Copolymerization of Anethole (M_2) and o-Chlorostyrene (M_1) at 70° C. (0.5% Benzoyl Peroxide)

Tube No.	Time, hr.	M_2[a]	Per cent chlorine in polymer	m_2[b]	Per cent conversion
A-1	18	0.933	18.82	0.251	0.5%
A-2	4.8	0.755	23.18	0.088	3.0
A-3	3.3	0.616	23.47	0.078	4.7
A-4	3.3	0.436	23.15	0.090	7.2
A-5	2.8	0.290	24.26	0.049	7.0
A-6	2.8	0.152	25.09	0.018	6.3

[a] Mole fraction of anethole in monomer mixture.

[b] Mole fraction of anethole in copolymer.

TABLE II. Acid-Catalyzed Copolymerization of Anethole (M_2) and o-Chlorostyrene (M_1) in CCl_4 at 0° C. (1% $SnCl_4$)

Tube No.	Time, hr.	M_2	Per cent chlorine in polymer	m_2	Per cent conversion
B-1	1.5	0.844	0.41	0.983	0.6
B-2	3.0	0.697	0.49	0.980	1.9
B-3	3.3	0.502	1.55	0.935	2.4
B-4	3.5	0.398	1.85	0.923	2.8
B-5	6.0	0.255	2.64	0.890	1.8
B-6	9.5	0.152	4.89	0.798	0.5
B-7	21.0	0.071	7.78	0.682	0.1

Experimental

Anethole (Paragon Testing Laboratories) was fractionally distilled, b.p. 94-95°/4.5 mm., m.p. 22-22.5°, $n_D^{25.5} = 1.5579$.

o-Chlorostyrene (Dow) was flash distilled, b.p. 46°/3 mm., $n_D^{25.5} = 1.5602$. Brooks (3) reported that $n_D^{20} = 1.5648$.

The acid-catalyzed polymerizations were carried out at 0°C. in a 20% solution in carbon tetrachloride. An ampul of stannic chloride was introduced into the monomer solution was the reaction tube sealed after freezing and evacuating. Vigorous shaking broke the ampul and caused the reaction to start. This technique will be described in detail in a later publication. The polymer product was isolated and purified by the usual method of successive precipitations in methanol. All samples were analyzed for chlorine.

The copolymer composition curves were plotted. For the acid catalyzed copolymerization the ratios of propagation rate constants were found to be $r_1 = 0.03$ ($\pm$ 0.005) and $r_2 = 18$ ($\pm$3). For peroxide catalysis $r_1 = 22$($\pm$8) and $r_2 = 0$ ($\pm$0.01). This means, for the former case, that anethole monomer is more reactive, with either anethole or o-chlorostyrene carbonium ion, than is o-chlorostyrene monomer. This might be expected because the presence of methyl and methoxyl groups increases the electron density at the double bond. In radical polymerization, anethole is much less reactive with an o-chlorostyrene radical and is very unreactive with an anethole radical.

The conclusion seems warranted that 1,2 disubstitution on the ethylenic double bond does not play as pronounced a steric role in ionic polymerizations as in the radical type.

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LETTER TO THE EDITORS

A NOTE ON THE OSMOMETRY OF POLYVINYL ACETATE-ACETONE SOLUTIONS

In "Intrinsic Viscosities and Molecular Weights of Polyvinyl Acetates," J. Polymer Sci., 2, 21-35, February, 1947, all values of μ_1 given for the system, polyvinyl acetate in acetone are incorrect. This fact, which was brought to the author's attention by Dr. L. A. McLeod, of the Canadian National Research Council, and to whom he is greatly indebted, was evidently the result of the accidental inclusion of a factor of 1/2 in the evaluation of the $RTd_1/M_1d_2^2$ term used in the calculation of the μ_1 values from the data. The values of $(1/2- \mu_1)$ calculated from the μ_1 values quoted in the paper are, therefore, too large by a factor of two.

At the time of the preparation of the original paper, a value of 1.14 grams per cc. was employed for the density of polyvinyl acetate (d_2) instead of the now more widely accepted value of 1.19 grams per cc. (cf. W. G. Wearmouth, J. Sci. Instruments, 19, 132, 1942), although this difference has only a slight effect on the resultant magnitude of μ_1.

The average of the μ_1 values reported for the polyvinyl acetate fractions was 0.387, whereas it should have been 0.444 or 0.439 depending upon whether the density of the polymer is taken as 1.14 or 1.19 grams per cc. The same error was automatically carried into the evaluation of μ_1 from the published data of Robertson, McIntosh, and Grummitt, Can. J. Research, B24, 150 (1946). The quoted average value of 0.377 should have been 0.438 or 0.433 depending upon the polymer density value used.

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REVIEW

"Crystalline Enzymes." Northrop, Kunitz, and Herriott. Columbia Univ. Press, New York, 1948, 352 pp., $7.50

This valuable contribution to enzyme chemistry from the laboratories of the Rockefeller Institute at Princeton is a timely successor to the book "Crystalline Enzymes" by Northrop, which appeared some ten years ago. As is indicated in the preface, the book, like its predecessor, is restricted to work carried out in the authors' laboratory and to related topics. This is at once both a source of strength and a defect: the former since the authors treat their material with unquestioned authority; the latter since a more comprehensive treatment of enzyme chemistry by these authors would be widely welcomed. Chapters on the general chemistry of enzymes, on pepsin, pepsinogen, chymotrypsinogen and chymotrypsin, trypsinogen, trypsin and trypsin inhibitor, carboxypeptidase and bacteriophage, existing also in the original book, have been enlarged and modernized. Corresponding with the development of the subject of crystalline enzymes, the following new chapters have been added: pepsin inhibitor, crystalline ribonuclease, crystalline hexokinase, and crystalline diphtheria antitoxin. This, the greater and most valuable part of the book, is concerned with the isolation, crystallization and purification of enzymes, precursors, and inhibitors, with their examination by various physical and analytical tools, and with the details of enzyme action.

Two further chapters, on the reaction of mustard gas with enzymes and on enzymes and the synthesis of proteins, are also included. In many ways these chapters are out of line with the rest of the book and presumably are included because their subject matter forms part of the program of work in the authors' laboratory. An appendix of some sixty pages, containing discussions on certain practical aspects of enzyme preparation and purification, and detailed experimental directions, adds considerably to the value of the book to the experimental worker. Indeed, as is later suggested, some of the material in the appendix could justifiably be included in the main text. A comprehensive list of references and index is provided.

Although the bulk of the material presented in the book has already appeared in original papers by the authors and others, the book attempts to fulfill an important function by collecting in 1 volume and coordinating so much related material. However, some criticism may justifiably be directed against the too-slavish following of the original manuscripts and the consequent lack of coordination. Thus it would have been in the interests of continuity if a discussion of the chief physical methods employed in examining enzyme and protein systems had been included at the beginning of the book rather than at scattered points in the text (e.g., pages 177, 192, 288). Further, in utilizing experimental data, diagrams and tables drawn from the original papers have not in many cases been sufficiently modified and labelled to make for clarity in their new surroundings, especially for those not directly working in the subject; it is hoped that in further editions this defect may be remedied.

In spite of minor points to be criticized, the book does provide a clear account of the physical and chemical investigation of a number of important crystalline enzymes, an account which should be of value not only to the enzyme chemist but to those in the neighboring fields of polymer chemistry. The reviewer has no hesitation, therefore, in commending it.

Paley Johnson

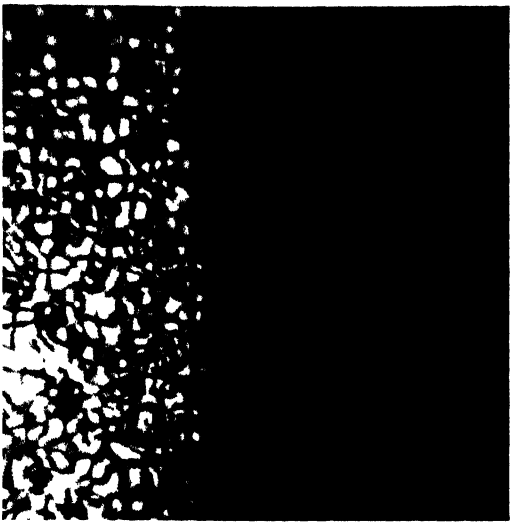

Plate II Decay of spherulites on heating polythene film Temperature rising from left to right of field (Crossed Nicols)

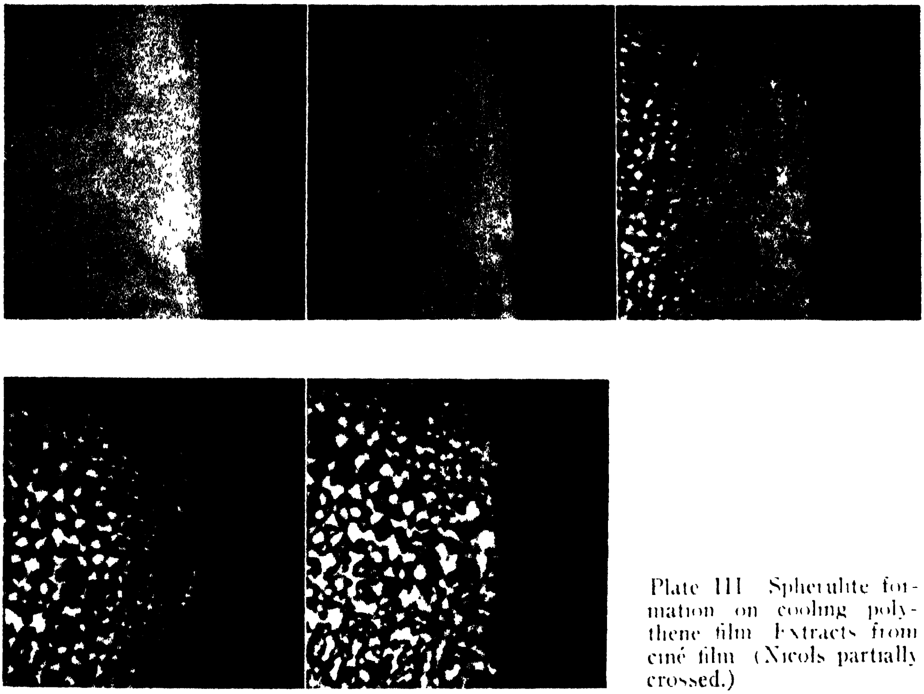

Plate III Spherulite formation on cooling polythene film Extracts from ciné film (Nicols partially crossed.)

S. W. HAWKINS and R. B. RICHARDS

Light Transmission and the Formation and Decay of Spherulites in Polythene, pages 515-522

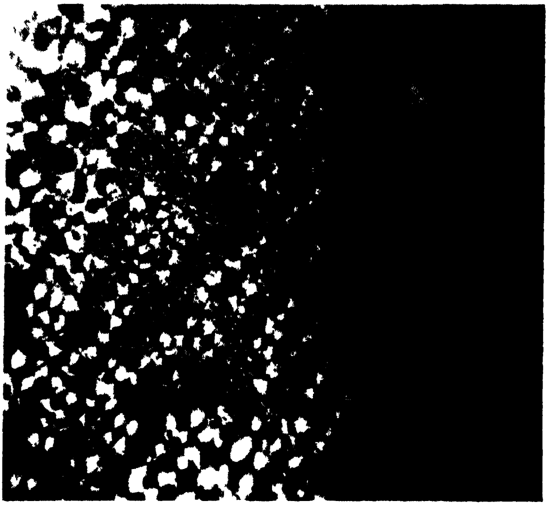

Plate IV Growth of spherulites from initial fine structure on cooling polythene film. (Nicols partially crossed.)

Plate V. Zone of fine structure formed by cooling after partial melting (Crossed Nicols.)

S. W. HAWKINS and R. B. RICHARDS

Light Transmission and the Formation and Decay of Spherulites in Polythene, pages 515-522

Journal of Polymer Science Vol. IV, pp. 545-554, 1949

Denaturation of Plant Proteins. II. Increase of Viscosity and Reducing Capability (Estimated by Titration with Iodine) Associated with Denaturation

B. JIRGENSONS,[1] *Department of Chemistry, Victoria University of Manchester, Manchester, England*

INTRODUCTION

In the previous article (part I) (1) it was stated that after denaturation of potato albumin and legumin the viscosity increases; simultaneously, there is an increase in the amount of iodine required for oxidation of the reducing groups of the denatured protein.

The experiments were continued, extending them to some other denaturing agents as sodium dodecylbenzene sulfonate, sodium salicylate, and the alcohols. The solutions of legumin in different salt solutions, such as potassium bromide, calcium chloride, potassium thiocyanate, magnesium nitrate, etc. were titrated with iodine; it was found that the amount of iodine required for oxidation is usually very low, with the exception of potassium thiocyanate solutions. Potassium thiocyanate denatures legumin like salicylate or dodecylbenzene sulfonate, increasing the viscosity as well as the amount of iodine required for oxidation. The influence of pH and temperature on the reaction with iodine was determined. The properties of deaminated legumin with respect to viscosity and reducing capability were investigated. Besides, it was found that ethyl and propyl alcohols of 2-30 volume per cent do not cause any denaturation of legumin, although the intrinsic viscosity of the solutions with salt, e.g., $CaCl_2$, and much alcohol is high. This indicates that the increase of viscosity in these cases is not due to the loosening and uncoiling of the compact legumin molecules, but to some other reasons. Thus, from the intrinsic viscosity only, there is no possibility of concluding anything about the transformation of globular particles in fibrous (as in the previous paper (1)) regarding the example of legumelin.

EXPERIMENTAL

Legumin used in the following experiments was extracted from green pea or horse bean meal. 700 g. of meal was treated at room temperature with 2 liters of 10% NaCl. After several days the solid was separated from the extract by filtration through a glass cloth. The filtrate was clarified by Sharples supercentrifuge (25,000 r.p.m.) and legumin precipitated by saturated ammonium sulfate. Mainly, 2-4 fractions were obtained. The number of fractions and the amount of each fraction depends upon the method of precipitation. If a saturated solution of ammonium sulfate is added until slight turbidity is evident, and after removing the first precipitate only a small surplus of salt is again added, four or even six fractions can be obtained; the two first fractions appear at 54-58% saturation, the third and fourth at 66-72%, and the last at about 80% saturation. If, however, so much ammonium sulfate is added that flakes appear in a half a minute, only two or three fractions can be separated. In the following experiments those fractions have been used which were precipitated by 66-72% saturation. The wet precipitates, containing ammonium sulfate, were dissolved in water and dialyzed; the globulins, which were precipitated were filtered off, redissolved in 10% NaCl, reprecipitated with ammonium sulfate, again dissolved in water, and dialyzed until no sulfate ions were detected in the dialyzing water. The pure white precipitates formed by the dialysis were filtered off and dried in a vacuum desiccator at room temperature. With respect to solubility and denaturation, there is no difference between the legumin of green peas and beans, but there are some differences between the fractions with respect to viscosity and reducing capability.

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The viscosity was determined by an Ostwald capillary viscometer (water number 188.6 sec.) at 25.0°C. The titrations were carried out with a solution of 0.002 *N* iodine in 0.2 *N* potassium iodide in the presence of starch until color appeared.

INFLUENCE OF pH AND TEMPERATURE ON IODINE REQUIRED FOR OXIDATION (2)

A soln. of 2% legumin in 10% NaCl was used. 10 cc. of this solution was mixed with 10 cc. of a McIlvaine buffer solution (x cc. 0.1 M citric acid with y cc. 0.2 *M* sec. sodium phosphate). These titrations were carried out at 15°C. The results are shown in Table I. It is obvious that between pH 5.0 and 5.8 the values are constant, but they decrease at a lower pH and increase rapidly at a higher pH. The solutions of legumin used formerly and also in the following experiments have had a pH of 4.9-5.9.

TABLE I Titration of Legumin with 0.002 Iodine at Different pH (t + 15°C.)

pH of mixture	Iodine required for 20 cc., cc.
4.0	1.05; 1.00
4.9	1.56; 1.58
5.4	1.60; 1.58
5.8	1.60; 1.63
6.2	1.80; 1.75
7.8	2.44; 2.50

The dependence of reducing ability on temperature is shown in Table II. It is obvious that at room temperature the values are almost independent of little variations of temperature, but they increase rapidly at above 25-30°.

DENATURATION BY POTASSIUM THIOCYANATE

The solutions of legumin in NaCl, KBr, KI, $CaCl_2$, or $Mg(NO_3)_2$ have a low reducing ability: for the oxidation of 10 cc. 1% legumin solution there was required (at 15°C. and pH 5.2-5.8) 0.8-1.0 cc. iodine for the once-reprecipitated fractions, and only 0.1-0.6 for the twice-reprecipitated fractions. However, the solutions of legumin in KCNS have a much higher reducing power. After subtraction of the amount required for the reduction of the solvent, there remains for legumin (10 cc. 1% solution) 3.2 cc. iodine. (These titrations were made at +5°C. It is noteworthy that the intrinsic viscosity of legumin in the case of potassium thiocyanate also is much higher than the viscosity in solutions with NaCl, KI, $CaCl_2$ or $Mg(NO_3)_2$. Some of the results are summarized in Table III.

TABLE II. Titration of Legumin at Different Temperatures; pH = 5.2

Temperature, °C.	Iodine required for 10 cc. of 1% legumin, cc.
5	0.80; 0.77
15	0.88; 0.90
25	0.90; 0.9[illegible]
30	1.75; 1.71
40	2.55; 2.53

TABLE III. Intrinsic Viscosity and Reducing Ability of Legumin in 4 M KCNS and 2 M $CaCl_2$

In 4 M KCNS			In 2 M $CaCl_2$		
c of legumin, g./l.	η_{sp}/c	Iodine for 10 cc., cc.	c of legumin, g./l.	η_{sp}/c	Iodine for 10 cc., cc.
20	0.037	6.4	20	0.0065	0.6
10	0.031	3.2	10	0.0060	0.3
5	0.028	-	5	0.0058	-
2.5	0.027	-	2.5	0.0058	-
1.25	0.027	-	1.25	0.0059	-

In this and all other tables the intrinsic viscosity is equal to η_{sp}/c; c (concentration) is expressed in g./liter, $\eta_{sp} = \eta_{rel} - 1$, or:
$c \rightarrow o$

$$\eta_{sp} = \frac{\text{Flowing time of legumin in solvent}}{\text{Flowing time of solvent}} - 1$$

LEGUMIN IN SOLUTIONS CONTAINING ALCOHOL

Many years ago the author found (3) that some nonsolvents of proteins, e.g., propyl alcohol, in the presence of high concentrations of salts, cause flocculation when the concentration of nonsolvent is 5-20% and above 60 volume per cent but at 35-55 volume per cent of propyl alcohol a strong peptizing action was observed. This was found at first in the case of casein, egg albumin, and hemoglobin, and later also with the potato proteins. It was found recently that a similar behavior shows legumin (the results concerning the flocculation will be published in another paper).

The question now arises as to whether or not the phenomena of coagulation at 5-20 volume per cent and peptization at 35-55 volume per cent are dependent on the denaturation of legumin. The titrations with iodine, which were carried out with several samples of legumin with calcium chloride, potassium iodide, and magnesium nitrate and 2-30 volume per cent of propyl alcohol showed that there is no denaturation (Table IV). The reducing ability of legumin at 5-10 volume per cent alcohol (where coagulation occurs) is the same as at 30 volume per cent (where the solution does not flocculate) and as low as when alcohol is not present.

TABLE IV. Viscosity and Reducing Ability of Legumin in Solutions Containing Salts and Propyl Alcohol

Solution	η_{sp}/c	Iodine required for 10 cc. 0.4% legumin in the solution of column 1, cc.
1. 0.4% legumin with 0.4 m./l. $CaCl_2$ and 2 vol. % alcohol	0.0052	0.22
2. 0.4% legumin with 0.4 m./l. $CaCl_2$ and 5 vol. % alcohol	0.0062	0.24
3. 0.4% legumin with 0.4 m./l. $CaCl_2$ and 30 vol. % alcohol	0.025	0.21
4. 0.4% legumin with 0.8 m./l. KBr and 5 vol. % alcohol	0.0050	0.20
5. 0.4% legumin with 0.8 m./l. KI and 10 vol. % alcohol	0.0055	0.24
6. 0.4% legumin with 0.4 m./l. $Mg(NO_3)_2$ and 2 vol. % alcohol	0.0052	0.18
7. 0.4% legumin with 0.4 m./l. $Mg(NO_3)_2$ and 30 vol. % alcohol	0.018	0.15

The titrations in these cases were carried out at +5°C., as were those solutions titrated without legumin, and the values mentioned in the Table IV represent differences in titration values of the solvent with legumin and in amount of iodine required for the solvent without protein. All the mixtures mentioned were only slightly opalescent, but some of them grew turbid with time.

Perhaps denaturation takes place at very high concentrations of the alcohols or at a higher temperature. The titrations with unheated mixtures containing 50-60% alcohol gave no definite answer to this question because of the difficulty of fixing the end-point of the reaction.

It is noteworthy that the viscosity of legumin in the solutions containing much propyl alcohol is high. Inasmuch as no denaturation can be proved, one can only conclude that in these cases the increase of viscosity is not due to any conversion of globular molecules into fibrous, but to the interaction of the legumin molecules with those of the components of the solvent, when a structuration gradually occurs. This is supported by the facts that viscosity increases with time when concentration of legumin is high enough (0.4%), but remains almost constant when the concentration is low (Table V).

TABLE V. Changes of Viscosity with Time for 0.4% and 0.1% Legumin in Solutions Containing Salt and Propyl Alcohol[a]

0.4% legumin with 0.8 m./l. KI and 40 vol. % alcohol		0.1% legumin with 0.4 m./l. $CaCl_2$ and 50 vol. % alcohol	
Hours	η_{sp}/c	Hours	η_{sp}/c
1/4	0.023	1	0.035
1	0.025	2 1/2	0.034
3	0.036	20	0.032
20	0.072	48	0.031
60	0.090	60	0.031

[a] A similar increase was observed with several other salts and with 35, 45, or 50 volume per cent propyl alcohol when the concentration of protein was not less than 0.2%

DENATURATION BY SODIUM SALICYLATE

Legumin dissolves easily in 3 *M* sodium salicylate. The solutions have a pH of 5.8-6.2 and are very viscous. The titrations with iodine showed that denaturation takes place (Table VI).

It is remarkable the η_{sp}/c increases with decreasing concentration of legumin. This indicates that, in the denaturation with salicylate, elongated heteropolar particles are formed, like the polyacrylic acids (4).

TABLE VI. Viscosity and Reducing Ability of Legumin in 3 M Sodium Salicylate Solution[a]

c of legumin, g./l.	η_{sp}/c	0.002 N iodine required for 10 cc., cc.
10	0.028	2.6
5	0.029	1.3
2.5	0.030	
1.25	0.032	
0.625	0.036	

[a] The intrinsic viscosity of the same legumin in 10% NaCl was 0.0040; the reducing ability, 0.6 cc. iodine for 10 cc. 1% legumin.

Although the intrinsic viscosity of legumin in salicylate is high, there is no increase in viscosity with time, and indication that the changes of viscosity in this case are not due to some structuration of the whole system, but to the conversion of globular particles in fibrous.

DENATURATION BY SODIUM DODECYLBENZENE SULFONATE (5)

This detergent (Santomerse No. 3, Monsanto), which has a long lyophobic chain, has a much stronger peptizing action on legumin than sodium salicylate, KI, or KCNS. Even a 0.5% solution of the detergent dissolves legumin easily. These solutions have a pH of 5.8-6.1, a high intrinsic viscosity, and higher reducing ability than solutions of legumin in KI or similar salt solutions. Some of the results are presented in Table VII.

TABLE VII. Intrinsic Viscosity and Reducing Ability of Legumin in Dilute Solutions of Sodium Dodecylbenzene Sulfonate (Santomerse)[a]

In 2% solution of Santomerse			In 0.5% solution of Santomerse		
c of legumin	η_{sp}/c	Iodine, cc.	c of legumin	η_{sp}/c	Iodine, cc.
10	0.016	1.5	10	0.011	1.6
5	0.017		5	0.010	
2.5	0.016		2.5	0.011	
1.25	0.015		1.25	0.010	

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[a] The amounts of iodine mentioned were required for 10 cc. 1% solutions; the same amount of legumin in 10% NaCl required 0.5 cc. iodine.

INTERACTION OF LEGUMIN WITH NITROUS ACID

It was found some years ago that proteins which are treated with nitrous acid in rather concentrated solutions of acetic acid are deeply denatured. For instance, deaminated albumins are insoluble in water and soluble only in alkalis, the solutions having high intrinsic viscosity (6). It was concluded that the formerly globular molecules of the spheroproteins by the treatment are converted into fibrous particles. Some measurements which were carried out by Professor W. W. Lepeschkin (University of Vienna, 1943) showed that some of the deaminated proteins have a greater molecular weight than the native proteins (unpublished results).

However, the results are very different when deamination is carried out in very slightly sour solutions. The deaminated products are then much more easily soluble, and there is no indication of a deep denaturation. This was found now in the cases of casein and also with legumin.

2 g. legumin was dissolved in 100 cc. 10% NaCl, 2 g. sodium nitrite; later, 10 cc. of 0.1 *N* acetic acid was added in small portions. After adding the acid, nitrogen bubbles appeared, but no precipitate was formed. After standing overnight at room temperature the clear solution was dialyzed in distilled water until no electrolytes could be detected in the water. During the dialysis a yellowish substance precipitated. This was filtered off and dried. Only 1.1 g. of the deaminated legumin was obtained. Some denatured albuminlike product remains in the filtrate (after dialysis); it flocculates by heating, like legumelin.

This mildly deaminated legumin dissolves easily in 10% NaCl, and these solutions differ only slightly in viscosity and reducing ability when compared with the native product. Some of the results are shown in Table III.

TABLE VIII. Viscosity and Reducing Ability of Deaminated Legumin and Legumin in 10% NaCl

Deaminated legumin			Legumin		
c of legumin, g./l.	η_{sp}/c	Iodine for 10 cc., cc.	c of legumin, g./l.	η_{sp}/c	Iodine for 10 cc., cc.
10	0.0067	0.28	10	0.0052	0.48
5	0.0078		5	0.0055	
2.5	0.0082		2.5	0.0050	

DISCUSSION AND CONCLUSIONS

In the previous paper (1) it was stated that the denaturation of the investigated plant proteins is connected with the increase of their viscosity. The reducing ability after denaturation increases approximately in the same proportion as the viscosity. Only in the case of legumelin, which is very probably a degradation product of legumin, is there a very high reducing ability, but the viscosity of the solutions is very low.

In the experiments described in this paper it was found that by denaturation the increase in viscosity parallels the increase in reducing ability when legumin is dissolved in solutions of potassium thiocyanate, sodium salicylate, and sodium dodecylbenzene sulfonate. However, with propyl alcohol (also with ethyl alcohol) and salt, which does not denature, the intrinsic viscosity is high, but the reducing power low.

The changes in shape of molecules of the dissolved proteins can be definitely determined only from measurements with very dilute solutions of the protein (see ref. 7). Thus, by considering the results shown in Tables III, VI, VII and VIII, there is almost no doubt that by denaturation with KCNS, sodium salicylate, and the detergent the globular molecules of legumin are either loosened and partly uncoiled or split into more elongated particles. Very important here also is the dependence of viscosity on the concentration of the protein: as seen from the tables, η_{sp}/c does not increase with concentration in the region of low concentrations; this is a proof that in the cases of KCNS, salicylate, and detergent no internal structuration takes place, although the viscosity of some of the solvents themselves (3 *M* sodium salicylate) is very high. Of course, it would be desirable to prove this with some other physical method, as the streaming birefringence.

Now, in the cases of 30-40% propyl alcohol and salt, at least at lower concentrations of alcohol, no denaturation takes place, yet the viscosity of the protein is high. One can only conclude that in these viscous solvents structuration takes place in the whole system. Some conclusions can also be made from the changes of viscosity with time at various concentrations of the protein. In the very viscous solutions with salicylate or urea (1) viscosity does not increase with time; it increases in the case of potato albumin in pyridine-water (1) or in the cases of propyl alcohol when the concentration of protein is high (0.4%), but does not increase when the concentration is small (0.1%, see Table V). Thus it may be concluded that despite the elongated (or loosened or branched) particles which may be assumed in the solutions of urea (1) or salicylate, there is no structuration, but it may occur in the solutions with pyridine (1) or with propyl alcohol and salt. Inasmuch as the reducing ability of legumin in the solutions containing alcohol is very low, it is possible that the reason for the high intrinsic viscosity lies in the interaction of the globular particles with the solvent, i.e., a continually building-in of the protein in the loose chains and nets of the solvent molecules.

In general, in the cases of viscous solvents and high intrinsic viscosity of protein there are three probabilities: (a) only change of shape occurs, (b) only structuration takes place, and (c) change of shape and structuration both occur. The solution of salicylate acts according to a; an example of type b is propyl alcohol (with salt); pyridine is perhaps an example of type c.

In the case of propyl alcohol and salt the increase of viscosity with time (Table V) occurs only when the concentration of protein is high; this increase is an introduction to gelation, and at still higher concentrations of legumin (0.8%) a very loose jelly is formed. That too is a proof that the cause of the increase is structuration, and at the same time a proof that the protein particles in this viscous system are globular, i.e., corpuscular, since in several instances with linear molecules a much smaller concentration of the colloid is needed for formation of jellies.

Acknowledgment

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Synopsis

Legumin of green peas and horse beans was dissolved in solutions of several salts and the viscosity and reducing capability of these solutions was determined. The amounts of iodine required for titration (reducing capability) are dependent on the pH of the solution and on the temperature; between pH 5.0 to 5.8 and +5° to +25° the titration values are almost constant. By comparing several neutral salts it was found that in the cases of sodium chloride, potassium bromide, potassium iodide, calcium chloride and magnesium nitrate the reducing capability and intrinsic viscosity of legumin both are low; however, in the case of potassium thiocyanate both values are high. No denaturation takes place in solutions containing 2-30% ethyl- or propylic alcohol and calcium chloride or like salts. Sodium salicylate causes denaturation; the intrinsic viscosity and reducing capability of legumin in these solutions is high. Sodium dodecylbenzene sulfonate has a strong peptizing action on legumin and denaturates it. After a mild deamination of legumin with nitrous acid only slight differences in viscosity and reducing capability could be observed. The solutions containing much propylic alcohol and salt grew in time more and more viscous, if the concentration of legumin was high, but remained of the same viscosity when the concentration of legumin was low. It was concluded that in these cases the high viscosity of legumin is due not to unfolding of the compact coils of native legumin, but to the interaction of the particles with the molecules of the solvent and to subsequent structuration. Loosening and transformation in more elongated particles may be assumed in the cases with thiocyanate, salicylate, and the detergent.

Résumé

La légumine des pois verts et des fèves a été dissoute dans de nombreuses solutions salines; la viscosité et le pouvoir réducteur de ces solutions ont été déterminés. La quantité d'iode, nécessaire à la titration (pouvoir réducteur) est fonction du pH des solutions et de la témperature; entre pH 5.0 et 5.8 et une température de 5° à 25°, ces valeurs titrimétriques sont la plupart constantes. En comparant l'influence de plusieurs sels neutres, tels le chlorure de sodium, le bromure et l'iodure de potassium, le chlorure calcique et le nitrate de magnésium, on constate que le pouvoir réducteur et la viscosité intrinsèque de la légumine sont faibles; en présence de thiocyanate de potassium, ces deux propriétés atteignent toutefois des valeurs élevées. Aucune dénaturation n'a lieu dans le cas des solutions contenant 2 à 30% d'alcool éthylique ou propylique et du chlorure calcique ou des sels similaires. Par contre le salicylate sodique entraine une dénaturation, et dans ce cas, la viscosité intrinsèque

et le pouvoir réducteur sont élevés. Le dodécylbenzène-sulfonate sodique exerce un effet peptisant énergique sur la légumine, et sa dénaturation. Par désamination faible de la légumine par l'acide nitreux, on n'observe que de faibles différences de viscosité et de pouvoir réducteur. Les solutions, contenant plus d'alcool propylique et de sels, deviennent de plus en plus visqueuses, si la concentration en légumine est élevée; elles restent, au contraire isovisqueuses si la concentration en légumine est faible. On conclut, que dans les cas de viscosités élevées de la légumine, cet effet n'est pas dû au déroulement des particules compactes de la légumine native, mais est dû à l'interaction de ces particules avec les molecules du solvant, suivies de structuration ultérieure. Un relâchement et une transformation en particules plus allongées peuvent être le résultat de l'action du thiocyanate, du salicylate et du détergent.

Zusammenfassung

Die Viscositaet und Reduzierfaehigkeit von Legumin gruener Erbsen und Bohnen wurde in einiger Salze ermittelt. Die fuer die Titrierung notwendige Iodmenge (Reduzierfaehigkeit) ist vom pH der Loesung und der Temperatur abhaengig; zwischen pH 5.0 und 5.8 und zwischen +5° und +25°C. ist der Titrations-Wert fast konstant. Beim Vergleich einiger Neutralsalze wurde gefunden, dass im Falle von Natriumchlorid, Kaliumbromid, Kaliumjodid, Calciumchlorid und Magnesiumnitrat die reduzierfaehigkeit und die Viskositaet des Legumins niedrig sind; im Falle von Kaliumthiocyanat waren beide Werte hoch. Keine Denaturierung wird in Loesungen die 2-30% Aethylalkohol oder Propylalkohol und Calciumchlorid oder aehnliche Salze enthalten, beobachtet. Natriumsalizylaet verursacht Denaturiurung; die Viskositaet und Reduktionsfaehigkeit des Legumins in diesen Loesungen ist hoch. Natriumbenzolsulfonat peptisiert Legumin und denaturiert sie. Nach einer schwachen Desaminierung der Legumin durch Salpetrige Saeure konnten nur kleine Unterschiede in Viskositaet und Reduzierfaehigkeit festgestellt werden. Die Loesungen, die viel Propylalkohol und Salz enthielten, wurden mit der Zeit zaeher, wenn die Konzentration, von Legumin hoch war; in Loesungen von niedriger Konzentration, blieb die Zaehigkeit unveraendert. Es wurde geschlossen, dass in diesen Faellen die hohe Viskositaet des Legumins nicht vom Aufwickeln des dichten Gewindes des natuerlichen Legumins, sondern von der gegenseitigen Einwirkung von Legumin und Loesungmittel-Molekuelen und der daraus folgenden Strukturierung, herruehren. Eine Lockerung und Umwandlung in laenglichere Teilchen kann in den Faellen von Thiocyanat, Salizylat und der Netzmittel angenommen werden.

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Thermodynamics of High-Polymer Solutions. III. Swelling of Cross-Linked Rubber[1]

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INTRODUCTION

The previous articles (1,2) in this series have dealt exclusively with the thermodynamic properties of solutions of more or less linear chain molecules. However, in many of the unvulcanized synthetics and in all vulcanized rubbers, these linear chains are bound together into a three-dimensional network structure, the chains being cross-linked by ordinary chemical bonds, either C-C bonds, or in the case of vulcanizates and oxidized rubbers, perhaps sulfur or oxygen bonds. One may in this case speak of the whole material as being one huge macromolecule with a molecular weight in astronomical figures.

A. THEORY

Flory and Rehner (3) have shown that if one assumes a simple tetrahedral network, one may derive an expression for the partial molal free energy of the solvent in the swollen network.

In the structure of Flory and Rehner, the network is assumed to consist of chains bound together in a repeating tetrahedral structure (somewhat like that of a diamond lattice) by $\nu/2$ cross-links, each cross-link joining four chains. Each chain is assumed to be like the linear chains discussed in Article I (1) with the exception that the two ends are bound.

Following Flory and Rehner, we represent the partial molal free energy of the solvent as the sum of terms for the free energy of mixing (dilution) and the free energy of elastic stretching.

$$\Delta\bar{F}_0 = \Delta\bar{F}_{mix} + \Delta\bar{F}_{el} = \Delta\bar{F}_{mix} + \Delta\bar{H}_{el} - T\Delta\bar{S}_{el} \tag{1}$$

The free energy of mixing is taken to be the same as that previously developed by Flory (4) and Huggins (5) for solutions of linear polymers, with the added condition that the molecular weight is, of course, infinite.

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[1] The major portion of the following work was done in 1943 on a grant from the Reconstruction Finance Corporation, Office of Rubber Reserve, for fundamental research in connection with the wartime synthetic rubber program.

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$$\Delta\overline{F}_{mix} = RT[\ln(1-\varphi_r) + \varphi_r + \mu\varphi_r^2] \qquad (2)$$

where φ_r represents the volume fraction of rubber and μ is a parameter which has been shown (1,5) to be derived from the entropy and heat of mixing such that:

$$\mu = \mu_s + \frac{V_0(\delta_0 - \delta_r)^2}{RT} \qquad (3)$$

The parameter μ_s is an entropy correction term of the order of 0.3 for most polymer solutions, and V_0 is the molal volume of the solvent. The quantity δ, which may be called (6) a "solubility parameter", is the square root of the "internal pressure" or "cohesive energy density", i.e., the energy of vaporization per cubic centimeter.[1]

$$\delta = (\Delta E^V/V)^{1/2} \qquad (4)$$

Flory and Rehner obtained for the elastic entropy $\Delta\overline{S}_{el}$, the expression:

$$\Delta\overline{S}_{el} = -\frac{RV_0\varphi_r^{1/3}}{V_c} = -\frac{R\varphi_r^{1/3}}{m_c} \qquad (5)$$

where V_c is the average molal volume of the chains between cross-linkages. Following the symbolism developed in Article I (1), we use m_c for the ratio V_c/V_0. The molecular weight between cross-links M_c is of course $V_c\ \rho_r$ where ρ_r is the rubber density.

The contribution of the heat of elastic deformation, if any, is unknown. Guth and his co-workers (7) have shown that in the case of mechanical stretching of rubber, the contribution of the heat to the total free energy does not exceed 5-10% and depends only slightly on the amount of stretching on swelling. In view of this observation and due to the lack of anything better, we may assume it to be negligible in comparison with the other terms:

$$\Delta\overline{H}_{el} \cong 0 \qquad (6)$$

Combining equations 2, 5, and 6, we obtain the Flory-Rehner equation:

$$\Delta\overline{F}_0 = RT[\ln(1-\varphi_r) + \varphi_r + \mu\varphi_r^2 + \frac{1}{m_c}\varphi_r^{1/3}] \qquad (7)$$

If we plot $\Delta\overline{F}_0$ as a function of φ_r, we find that in contradistinction to non cross-linked polymers, the free energy increases initially so that the free energy-volume fraction curve has a positive slope at $\varphi_r = 0$ and reaches a maximum before decreasing regularly to $-\infty$, as shown graphically in Figure 1. The appearance of a maximum in a free energy-composition diagram requires that the components exhibit partial miscibility. Furthermore, compositions in which the partial molal free energy of the solvent in the solution is greater than that of the pure solvent are necessarily excluded. Hence, one of the phases must be pure solvent, and the other will have the composition corresponding to the intersection of the curve with the $\Delta\overline{F}_0 = 0$ ordinate.

We conclude from this that the solubility of the cross-linked network in the solvent is exactly zero, complete miscibility (or even

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[1] Note that we use δ in place of the α of Article I (1).

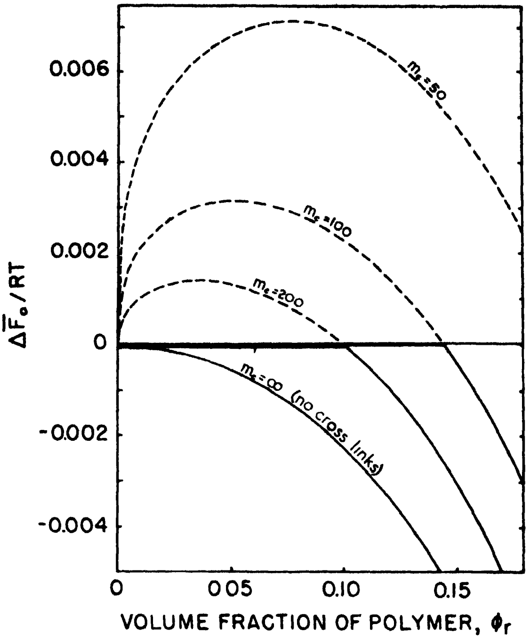

Fig. 1. Free energy relations in cross-linked systems.

partial solubility) being prevented if the polymer is at all cross-linked, no matter how loosely.

Similarly the polymer itself will exhibit only a limited swelling in even the "best" solvent (for which $\mu \sim 0.3$), a swelling which can be calculated from these thermodynamic considerations.[1]

The condition for swelling equilibrium is that the free energy of the solvent in the swollen polymer equal that of the pure solvent outside, that is to say, the partial molal free energy of dilution must be zero.

$$\Delta\bar{F}_0 = 0 \tag{8}$$

Therefore from equation 7:

$$\ln(1 - \varphi_r) + \varphi_r + \mu\varphi_r^2 + \frac{1}{m_c}\varphi_r^{1/3} = 0 \tag{9}$$

If μ, V_0 and V_c are known, φ_r is uniquely determined and one can plot it as a function of the variables μ and m_c. However, a more direct method of expressing the degree of swelling is as the maximum imbibition Q, volume solvent imbibed per unit volume polymer. Q is by definition related to φ_r in the following manner:

$$Q = \frac{1 - \varphi_r}{\varphi_r} \qquad \varphi_r = \frac{1}{Q + 1} \tag{10}$$

Figure 2 gives Q as a function of μ and m_c.

B. SWELLING OF VULCANIZATES

In order to check the applicability of the theory of Flory and Rehner, as developed in the preceding pages, we have measured in this laboratory the swelling in thirteen different organic solvents of the gum stocks of twelve different rubbers–Hevea (Natural rubber or polyisoprene), polybutadiene, five butadiene-styrene copolymers, Neoprene, and four butadiene acrylonitrile copolymers.

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[1] A notable attempt to explain the variation of swelling with the solvent was made earlier by G. Gee (8).

1. Experimental Procedure

The vulcanizates used in this research were obtained from The Firestone Tire and Rubber Company; the compounding and curing formulas are given elsewhere (9). For the GR-S vulcanizates (75% butadiene, 25% styrene), the symbols L, M, and H refer to low, medium, and high percentage conversion of monomer to polymers; this increasing degree of conversion may be correlated with increasing gel formation (10). The symbols attached to the acrylonitrile copolymers (Buna N's) have the following significance: NM—modifier used; lfa—low fatty acid content; N—modifier absent; NX—excess of acrylonitrile added.

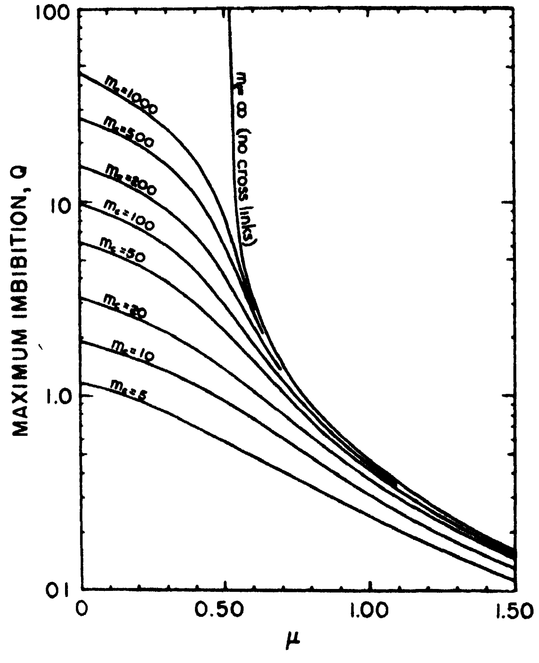

Fig. 2. Equilibrium swelling as a function of μ and m_c.

Following a procedure similar to that of Whitby (11), rectangular pieces of vulcanizates weighing approximately 0.1 g. (25 mm. x 4 mm. x 1 mm.) were placed in corked test tubes containing 15 cc. of solvent and allowed to swell at room temperature. Every two or three days the samples were taken out, their surfaces rapidly dried with filter paper, the samples weighed and then replaced in the corked test tubes. In the case of hevea, polybutadiene and Buna S rubbers, the weight of the swollen pieces had reached a maximum value after about five days and did not change appreciably for the next four days. From the weight increase and the density of the solvents the volume of absorbed liquid was calculated.[1]

In the case of the Buna N type rubbers and neoprene, a slow increase of Q with time was observed in some solvents. Presumably two processes are going on simultaneously: the rapid imbibition of solvent by the rubber, until swelling equilibrium is reached (as defined by equation 8); and the slow oxidative breakdown of primary bonds (12) resulting in an increase of V_C and hence of the swelling.

Errors due to this[2] were avoided by measuring the swelling at different time intervals until only the slow increase is observed, and plotting the volume fraction φ_r (calculated from the Q's) against the time t (Fig. 3.). By extrapolating to zero time, one can determine the equilibrium swelling independently of the oxidative breakdown. The Q's in Table I were calculated back from such extrapolated φ_r's.

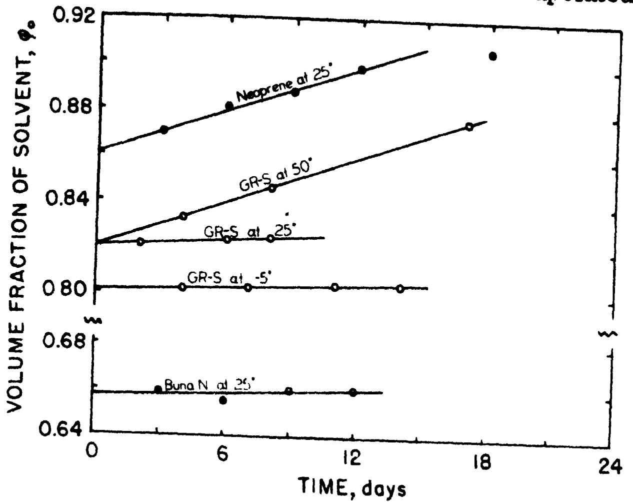

Fig. 3. Swelling in ethyl benzene as a function of time, showing extrapolation to zero time.

The solvents used are commercial solvents, dried in the laboratory. The densities of the polymers were determined with a pycnometer at 25°C. No thermostat was used for the swelling measurements but

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[1] In reality, the density of the solvent in the swollen network is greater than that of the pure solvent, for it is under considerable pressure. We have, however, neglected this factor, which is ordinarily quite small, in calculating Q.

[2] G. Proske has noted [Gummi-Zeitung, 54, 141-2, 167-8 (1940); Chem. Abstracts, 34, 6845 (1940)] that swelling values in two liquids may vary much more after short times of treatment than after prolonged treatment, and that differences in swelling values at different temperatures become greater with prolongation of time of treatment. The former observation can be attributed to failure of the swelling processes to reach equilibrium at short times. The latter observation becomes understandable in terms of the oxidative breakdown of primary bonds; there is no reason why the rate constant of this reaction and its temperature coefficient should not vary from solvent to solvent. As seen in Figure 3, this seems to be the case.

TABLE I. Maximum Imbibition Q For Various Rubber-Gums at 25° C.

Number	198	214	200	206	202	208	204	216	210	226	218	212
	Hevea	Polybutadiene	Buna S					Neoprene	Buna N			
Composition	--	100% B	85B 15S	75B 25S^L	75B 25S^M	75B 25S^H	60B 40S	GN	NM	NM 1fa	N	NX
Solvent												
n-Hexane	2.15	1.40	1.06	1.41	1.13	1.06	1.01	0.26	0.10	0.17	0.15	0.06
n-Heptane	2.27	1.48	1.15	1.60	1.14	1.08	(0.92)	0.21	0.04	0.11	0.04	0.05
"Octanes"	3.20	2.14	1.69	3.20	2.03	1.69	1.87	0.45	0.13	0.21	0.13	0.05
Cyclohexane	4.05	3.05	2.75	5.54	3.26	2.76	4.00	1.32	0.26	0.34	0.28	0.10
Carbon tetrachloride	5.62	4.35	4.34	10.5	5.29	4.35	6.52	4.95	1.11	1.27	1.00	0.61
p-Xylene	5.57	3.81	3.95	7.53	4.68	3.81	6.25	5.58	1.70	2.10	1.45	0.90
Ethylbenzene	5.02	3.63	3.57	7.39	4.52	3.83	5.75	6.20	1.93	2.28	1.41	0.96
Toluene	4.59	3.91	3.87	7.92	4.74	3.87	6.40	5.58	2.06	2.56	1.49	1.19
Benzene	4.13	3.51	3.42	7.20	4.59	3.77	6.25	5.66	1.63	2.78	1.69	1.87
Chloroform	5.71	4.50	4.50	8.52	5.53	4.62	7.25	6.41	4.53	4.68	3.17	3.68
Chlorobenzene	-	-	-	-	-	-	-	7.55	3.88	4.62	2.22	3.12
Nitrobenzene	1.06	0.92	1.25	2.44	1.78	1.53	3.01	3.98	3.71	3.61	2.10	2.37
Dioxane	1.64	1.32	1.53	2.85	2.05	1.73	3.26	4.00	2.75	2.72	1.74	2.03

the room temperature (about 24°C.) varied by less than 3°C.

The precision is probably no better than 1-2%.

2. Results

The data obtained are tabulated in Table I in terms of the maximum imbibition Q, the solvents and the rubbers being arranged in order of increasing δ's.

3. Calculation of V_c for the Nonpolar Rubbers

By rearranging equation 9, one obtains an explicit equation for V_c, the average molal volume between cross-links, in terms of the φ's obtained by swelling measurements:

$$V_c = -\frac{V_0\varphi_r^{1/3}}{\ln(1-\varphi_r) + \varphi_r + \mu\varphi_r^2} \tag{11}$$

To make such a calculation, we must utilize equation 3, which requires a knowledge of δ_0, and δ_r. δ_0 is calculated from standard thermodynamic data on heats of vaporization at 25°C.; the values are rounded off to units of 0.05; for these experiments, greater precision is not justified. They are known for the above solvents.[1] No reliable data for the heat of vaporization at 25° exist for dioxane or nitrobenzene. In addition, the solvent "octanes" used was a commercial solvent of uncertain composition. We eliminate these three temporarily and calculate V_c for the nonpolar rubbers from the remaining time (there were no measurements of these rubbers in chlorobenzene), choosing a value of δ_r to give the smallest root mean square error. The results are shown in Table II. The agreement is quite good considering the errors of measurement, and the sensitivity of equation 11 to slight errors in φ_r or μ.[2]

The values of V_c are consistently low for cyclohexane and consistently high for chloroform. A reasonable explanation would be that the assumption of a constant μ_s is too general: there is good evidence, both theoretical (13) and experimental (14), for some variation in μ_s, both from solvent to solvent and from polymer to polymer.

It should be noted that the δ_r values are entirely reasonable: the butadiene rubbers increase regularly with increasing styrene content as is to be expected from the higher position of aromatic compounds in the internal pressure scale.

4. Estimation of δ_0 from Swelling Data

If V_c and Q are known, one may reverse equation 8 to calculate μ, and if δ_r is known, use equation 10 to estimate δ_0 for a solvent

[1] Since the original publication of this research as a wartime report to the Polymer Research Board, the data have been recalculated to conform with the latest thermal data on the hydrocarbons, "Selected Values of Properties of Hydrocarbons," Bureau of Standards Circular C461 (Washington, 1947).

[2] Equation 11 is especially sensitive for large values of μ, since the denominator in these cases is the small difference of two large numbers, the difference being as low as 1% of the two values.

TABLE II. Molal Volume between Cross-Links V_c for Nonpolar Rubbers (Determined from Swelling Data)

Rubber		198	214	200	206	202	208	204
		Hevea	Poly-butadiene	Buna S				
Solvent				85B 15S	$75B_L$ 25S	$75B_M$ 25S	$75B_H$ 25S	60B 40S
	δ	8.35	8.45	8.55	8.60	8.60	8.60	8.70
n-Hexane	7.3	8,800	4700	3700	17,500	5400	4700	10,100
n-Heptane	7.45	8,000	4200	3700	13,000	4100	3500	3,900
Cyclohexane	8.2	6,000	3800	3400	11,000	4600	3500	6,800
Carbon tetrachloride	8.5	8,900	5800	5800	24,500	8000	5800	11,500
p-Xylene	8.8	13,200	7000	6600	19,000	8600	6100	13,300
Ethylbenzene	8.8	10,900	6500	5600	18,000	8100	6100	11,600
Toluene	8.9	8,600	6500	5800	22,000	7800	6200	12,700
Benzene	9.15	7,700	5400	4500	15,000	7100	5100	11,300
Chloroform	9.25	13,400	7500	6600	19,000	9200	6800	13,600
Average		9,500	5700	5100	17,700	7000	5300	10,500
Probable error of the mean, %		5.9	4.7	5.6	5.4	5.9	5.1	7.5

for which reliable thermodynamic measurements are lacking. We shall use such a procedure to estimate δ_0 values for nitrobenzene, dioxane, and "octanes." We obtain seven values for each, one from each of the rubbers for which we have determined δ_r and V_c. Table III shows the results. These correspond to heats of vaporization ΔH^V at 25°C. of 9.2 kcal. for dioxane, 10.7 kcal. for nitrobenzene, and 10.3 kcal. for "octanes."[1]

We shall round off these δ_0 values to 10.0, 9.9 and 7.7, respectively, and use them for calculations of V_c for polar rubbers.

5. Calculation of V_c for the Polar Rubbers

The five polar vulcanizates present an additional problem. The polarity which we have ignored (without justification) for polar solvents such as nitrobenzene cannot be ignored for Buna N rubbers which contain appreciable polar CN groups. No adequate treatment of the heat of mixing of polar substances exists, although internal pressure must play some role. Since a satisfactory theoretical expression is lacking, we have adopted the empirical expression proposed in Article I:

$$\mu = \mu_s + \frac{KV_0(\delta_0 - \delta_r)^2}{RT} \qquad K > 1 \qquad (12)$$

---

[1] Since these values may involve an implicit correction for polarity, they should not be taken too seriously, especially that for nitrobenzene.

Using equation 12, we have calculated V_c for the five polar rubbers, choosing values of K and δ_r such as to minimize the mean square error. As noted earlier, equation 11 is extremely sensitive to small errors when μ is large, so solvents for which μ exceeded 0.8 were not used in calculating V_c. Table IV shows the results for the five polar rubbers.

TABLE III. Estimation of δ_o from Swelling Data

Rubber	Dioxane	Nitrobenzene	"Octanes"
198	9.93	9.94	7.70
214	10.05	10.05	7.71
200	10.02	9.99	7.67
206	9.96	9.88	7.75
202	9.97	9.90	7.73
208	10.01	9.92	7.81
204	9.90	9.79	7.70
Average	9.98	9.92	7.72

TABLE IV. V_c for Polar Rubbers

		216	210	226	218	212
Rubber		Neoprene GN	Buna N			
			NM	NM 1fa	N	NX
	δ_r	9.25	9.5	9.5	9.5	9.6
Solvent	δ_o K	1.0	2.1	2.1	2.1	2.7
Cyclohexane	8.2	1,700	-	-	-	-
Carbon tetrachloride	8.5	10,800	2700	4700	2300	2900
p-Xylene	8.8	13,100	4000	6100	2900	2600
Ethylbenzene	8.8	15,500	5200	7300	2800	3100
Toluene	8.9	10,300	3300	6600	1900	2400
Benzene	9.15	8,300	1300	3100	1400	1900
Chloroform	9.25	9,100	5500	5800	3100	4400
Chlorobenzene	9.5	15,400	5100	6600	2100	3600
Nitrobenzene	9.9	7,300	3300	5600	1600	2700
Dioxane	10.0	6,100	5900	3200	2400	1700
Average		9,800	4000	5400	2300	2800
Probable error of the mean, %		12.0	8.5	6.2	5.8	6.7

Except for Neoprene in cyclohexane, the agreement is fairly good. Rather striking is the fact that the best fit[1] for neoprene is given with K = 1.0, implying that Neoprene behaves like a nonpolar rubber.

Table V shows the swelling Q calculated for these poor solvents for which V_c could not be calculated in Table IV.

TABLE V. Swelling in Poor Solvents

Solvent	μ	m_c	$Q_{calc.}$	$Q_{obs.}$
216 - Neoprene GN $V_c = 9800$				
n-Hexane	1.13	75	0.31	0.26
n-Heptane	1.10	67	0.33	0.21
Octanes	0.95	60	0.48	0.45
210 - Buna NM $V_c = 4000$				
n-Hexane	2.52	30	0.04	0.10
n-Heptane	2.46	27	0.04	0.04
Octanes	2.15	25	0.06	0.13
Cyclohexane	0.94	37	0.46	0.26
226 - Buna NM 1fa $V_c = 5400$				
n-Hexane	2.52	41	0.04	0.17
n-Heptane	2.46	37	0.04	0.11
Octanes	2.15	33	0.06	0.21
Cyclohexane	0.94	50	0.48	0.34
218 - Buna N $V_c = 2300$				
n-Hexane	2.52	18	0.04	0.15
n-Heptane	2.46	16	0.04	0.04
Octanes	2.15	14	0.06	0.13
Cyclohexane	0.94	21	0.42	0.28
212 - Buna NX $V_c = 2800$				
n-Hexane	3.42	21	0.015	0.06
n-Heptane	3.36	19	0.015	0.05
Octanes	2.94	17	0.02	0.05
Cyclohexane	1.26	26	0.22	0.10

C. RELATION OF THE ELASTIC MODULUS TO THE MOLECULAR VOLUME BETWEEN CROSS-LINKS, V_c

In recent years we have seen the development of an extensive theory of elasticity for cross-linked polymers, contributed largely by Wall (15), James and Guth (16), Flory and Rehner (17), and Treloar (18).

According to these theories, we may regard the rubber network as a cube incompressible, but capable of distortion under stress to a

[1] Contrary to appearances, better agreement is not obtained for Neoprene by increasing K and increasing δ_r. This, it is true, increases V_c for cyclohexane, but at the same time throws xylene, ethylbenzene and chlorobenzene farther out of line.

parallelepiped of dimensions L_x, L_y, L_z with $L_x = L_y$. According to the assumption of incompressibility:

$$L_x^2 L_z = 1 \tag{13}$$

Assuming that the chains follow a Gaussian distribution, and with a reasonable theory which considers only the distribution between the ends of the chains (i.e., the linkage), we find for the tension Z,

$$Z = \frac{RT}{V_c}[L_z - \frac{1}{L_z^2}] \tag{14}$$

where L_z is, of course, the extension in the direction of stretch. Similarly the differential Young's modulus:

$$E = \frac{dZ}{dL_z} = \frac{RT}{V_c}[1 - \frac{2}{L_z^3}] \tag{15}$$

Further, if the stress is referred to the actual cross section, we obtain still a third modulus:

$$\tau = \frac{Z}{L_x^2} = ZL_z = \frac{RT}{V_c}[L_z^2 - \frac{1}{L_z}] \tag{16}$$

This latter quantity τ has been measured in the Physics Research Laboratory of The Firestone Tire and Rubber Company, on the same samples of vulcanizates on which our swelling measurements were made. Measurements were made a few seconds after stretching to 100% elongation ($L_z = 2$) at 40°C. In this case:

$$\tau = \frac{3.5RT}{V_c} \tag{17}$$

or, expressing the results in pounds per square inch:

$$\tau = \frac{1.326 \times 10^8}{V_c} \text{ p.s.i.} \tag{18}$$

Table VI and Figure 4 compare values of τ calculated in this way with the experimentally observed values.

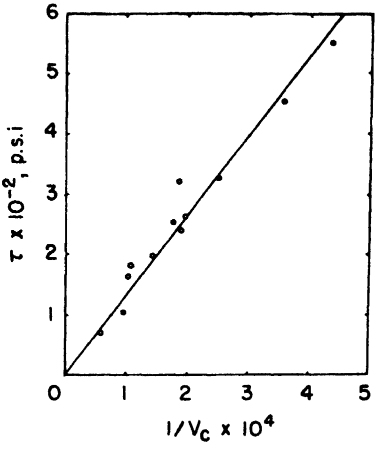

Fig. 4. The relation between cross-linking and the elastic modulus.

TABLE VI.

Polymer	No.	V_c	ρ_r	M_c	$\tau_{calc.}$	$\tau_{obs.}$	Error, %
Hevea	198	9,500	0.967	9,200	140	182	-23
Polybutadiene	214	5,700	0.976	5,600	233	254	- 8.3
Buna S							
85/15	200	5,100	0.985	5,000	260	264	- 1.5
75/25 low	206	17,700	0.997	17,600	75	69.1	8.5
75/25 med.	202	7,000	1.01	7,100	189	198	- 4.5
75/25 high	208	5,300	1.018	5,400	250	241	3.7
60/40	204	10,500	1.021	10,700	126	104	21
Neoprene GN	216	9,800	1.27	12,400	135	164	-18
Buna NM	210	4,000	1.02	4,100	332	327	1.5
Buna NM lfa	226	5,400	1.004	5,400	245	322	-24
Buna N	218	2,300	1.01	2,300	577	551	4.7
Buna NX	212	2,800	1.054	2,900	474	453	4.2

The average error is only 10%, and the maximum error 24%. Considering the limitations of the theory, the errors of measurement, etc., this is remarkably good.

D. ANALYSIS OF EXISTING DATA ON THE SWELLING OF VULCANIZATES (NATURAL RUBBER)

In view of the success achieved in applying the theories of Flory and Rehner to the swelling measurements made in this laboratory, it is of interest to attempt to apply this treatment to some of the swelling data existing in the literature.

By far the largest amount of data reported to date is that on the swelling of natural rubber in various solvents accumulated by Whitby and co-workers (11). We may assume that the value of δ_r is 8.35, the same as that of the Firestone Hevea sample measured in this laboratory, since δ_r depends only on the microstructure of the polymer. V_c depends upon the degree and method of vulcanization, and so must be redetermined from this sample. This value was calculated for benzene (7100), and toluene (7100), giving an average of 7100.

Taking V_c as 7100 and the values of δ_0 and V_0 calculated from thermodynamic data, Q was calculated for a variety of solvents and is compared with Whitby's experimental data in Table VII.[1]

---

[1] Calculations of Q were made only for those solvents for which δ_0 could be determined from existing data on heats of vaporization or vapor pressures. Hence only a small fraction of the experimental data is represented in Table VII. Approximate calculations of δ_0 from the boiling point using the "Hildebrand rule" yield good agreement between $Q_{obs.}$ and $Q_{calc.}$ for nonpolar solvents, but the uncertainty of the "rule" does not warrant their inclusion here.

TABLE VII. Swelling of Natural Rubber in Various Solvents ($\delta_r = 8.35$, $V_c = 7100$)

Solvent	V_o	δ_o	μ	m_c	$Q_{calc.}$	$Q_{obs.}$
Hydrocarbons						
n-Pentane	116	7.05	0.63	61	1.4	1.12
n-Hexane	131	7.3	0.54	54	1.8	1.18
n-Octane	164	7.55	0.475	43	2.1	2.34
Benzene	89	9.15	0.40	80	3.9	3.95
Toluene	107	8.9	0.35	66	4.1	4.10
m-Xylene	123	8.8	0.34	58	3.8	4.15
Mesitylene	140	8.8	0.35	51	3.4	3.25
Limonene	162	8.5	0.30	44	3.5	4.00
Methylcyclohexane	128	7.8	0.36	55	3.5	2.60
Ketones						
Acetone	74	9.9	0.60	96	1.8	0.03
Methyl ethyl ketone	90	9.3	0.44	79	3.3	0.71
Diethyl ketone	106	8.8	0.34	67	4.1	1.6
Diisopropyl ketone	142	7.6	0.44	50	2.6	1.9
Cyclohexanone	104	9.9	0.72	68	1.0	(2.6)
Alcohols						
n-Propyl alcohol	75	11.9	1.9	95	0.09	0.02
tert-Butyl alcohol	95	10.6	1.0	75	0.43	0.13
Amyl alcohol	108	10.9	1.5	66	0.16	0.07
n-Hexyl alcohol	124	10.7	1.45	57	0.17	0.15
n-Heptyl alcohol	141	10.6	1.5	50	0.16	0.65
n-Octyl alcohol	157	10.3	1.0	45	0.40	0.85
Nitriles						
Acetonitrile	53	11.9	1.4	134	0.19	0.04
Propionitrile	71	10.6	0.9	100	0.58	0.06
Capronitrile	120	9.4	0.52	59	2.1	0.70
Benzonitrile	103	8.35	0.30	69	4.6	2.0
Nitro Compounds						
Nitromethane	54	12.7	2.0	131	0.08	0.03
Nitrobenzene	103	9.95	0.74	69	0.94	1.15
Acid Chlorides						
Acetyl chloride	71	9.5	0.48	100	3.2	(<5.1)

The agreement is excellent in the case of the hydrocarbons and good in the case of the alcohols—expecially considering the uncertainty as to the heats of vaporization of the higher alcohols.

In the case of ketones and nitriles, all highly polar solvents, the $Q_{calc.}$ is invariably higher than $Q_{obs.}$ as would be expected from the theory of the heat of mixing.

Until one finds a way to treat polar solvents, calculation of φ_r by equation 9 gives only a lower limiting value—and hence such calculations of Q for polar solvents yield only upper limits to the swelling.

It is of interest to note, however, that both $Q_{obs.}$ and $Q_{calc.}$ fall in the same relative order in the two homologous series, indicating that the underlying principles are probably sound.

E. RELATION OF V_C TO THE SULFUR CONTENT OF VULCANIZATES

An interesting comparison of the amount of cross-linking with the sulfur content of vulcanizates is provided by the data of Zhukov and Simkhovich (19) on the Russian SK (sodium polymerized polybutadiene) in toluene. We have taken their data[1] on the swelling of polymers of different sulfur contents and calculated values of V_C as shown in Table VIII.

TABLE VIII. Swelling of Russian SK as a Function of Sulfur Content.

Sulfur added, wt. %	Q	φ_r	V_c	$\nu = \frac{1}{V_c}$
2	5.0	0.167	8000	1.2×10^{-4}
4	3.5	0.222	4600	2.2
6	2.5	0.286	2700	3.7
12	1.65	0.378	1430	7.0
24	0	1.0	(0)	-

We have assumed a value of $\mu = 0.3$, since the heat of mixing must be virtually negligible.[2]

In the last column, ν represents the reciprocal of the average molecular volume between cross linkages, that is the moles of chains per cubic centimeter. If ν is therefore a measure of the number of cross links, it should be proportional to the amount of sulfur added. Figure 5 shows that this relation is approximately true; ν varies almost linearly with the sulfur content. The failure of the 24% sulfur polymer to show any swelling (and hence its departure from the linear relation) may be attributed to the fact that with the very tightly cross-linked structure, the molecular volume between cross-linkages is small (ca. 700). The chains are short, and the resultant "holes" in the network may be too small to accomodate the molecules of solvent. In such a case, swelling, while thermodynamically possible, is mechanically impossible.

From the data of Table VIII, one may calculate that there are approximately 3×10^{-3} moles of cross-links ($\nu/2$) per gram of sulfur or 0.1 cross-links per atom of sulfur.[3]

[1] Their data are expressed in the form of graphs, so the values given in Table VIII are only approximate.

[2] For emulsion polymerized polybutadiene, we have found $\delta_r = 8.45$ (Table II). It cannot be emphasized too strongly, however, that the Russian SK produced by sodium polycondensation is radically different in almost every particular. A value of $\delta_r = 8.6$-8.7 would seem to fit solubility data and is in agreement with the large amount of 1,2 addition attributed to it. For such an δ_r, μ_H is virtually zero and $\mu \cong \mu_S \sim 0.3$.

[3] We have calculated the above data for $\mu = 0.25$ and 0.35, and the linear relation is preserved, although the slope of the line is shifted. Specifically, for $\mu = 0.25$, we obtain a value of 0.12 cross links per atom of sulfur; for $\mu = 0.30$, 0.10; and for $\mu = 0.35$, 0.08.

Evidently, in this polymer, at least, one cross-link is formed by every eight to twelve sulfur atoms, on the average. Since crystalline sulfur is S_8 and liquid sulfur largely so, one might assume that one cross-link is formed for every sulfur molecule added.[1] A value of 0.125 cross-links per atom of sulfur would be within the limit of error of the experiments, but more data, especially on other vulcanized polymers would be required before attempting any definite conclusions.

Very recently, Pasternak and Kuhn have studied the variation of V_C with degree of vulcanization by measuring the swelling of rubber in four different solvents (20).

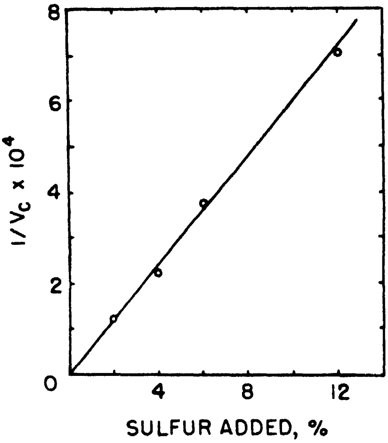

Fig. 5. Cross-linking as a function of sulfur content.

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The authors wish to thank Professor Hugh S. Taylor for his continuing interest and encouragement in this research; Professor Arthur V. Tobolsky for numerous discussions of the theories of elasticity and swelling; The Firestone Tire and Rubber Company, in particular Drs. J. H. Dillon and I. B. Prettyman, for supplying rubber samples and measuring the elastic modulus; Messrs. R. A. Miller, B. F. Burns, and R. L. Gensler for some of the experimental swelling measurements; and the Reconstruction Finance Corporation (Office of Rubber Reserve) for sponsorship of the research program.

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[1] This would not necessarily involve the incorporation of the sulfur into the rubber molecule, but merely its participation in the formation of the cross-link. Nor is a cross-link necessarily a single bond; the several adjacent bonds which might be produced in a rapid chain reaction might constitute effectively only one cross-link.

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Synopsis

The equilibrium swelling of the gum stocks of twelve different rubber vulcanizates has been measured in thirteen organic solvents. The results are in good agreement with the theory of Flory and Rehner. Values of the internal pressure (cohesive energy density) and the average molal volume between cross-linkages V_c have been determined for the rubbers. The molal volume V_c is shown to agree closely with that obtained from measurement of the elastic modulus. An analysis of earlier data on the swelling of polybutadiene shows the number of cross-linkages to be directly proportional to the sulfur content.

Résumé

L'équilibre de gonflement d'échantillons de douze différents caoutchoucs vulcanisés a été mesuré en presence de treize solvants organiques. Les résultats sont en bon accord avec la théorie de Flory et de Rehner. Les valeurs des pressions internes (densité d'énergie de cohésion) et le volume molaire moyen entre les pontages V_c ont été déterminées pour ces caoutchoucs. Le volume molaire V_c concorde sensiblement avec celui déterminé par des mesures du module d'élasticité. L'analyse de données antérieures, concernant

le gonflement du polybutadiène, indique un nombre de pontages, directement proportionnel à la teneur en soufre.

Zusammenfassung

Die Gleichgewichtsquellung der Gummiharze von zwoelf verschiedenen Gummivulkanisaten wurde in dreizehn organischen Loesemitteln gemessen. Die Ergebnisse stimmen gut mit Flory und Rehner's Theorie ueberein. Werte des inneren Druckes (Cohaesionskraftdichte) und des durchschnittlichen molalen Umfangs zwischen Vernetzungspunkten V_c wurden fuer die Gummiproben bestimmt. Der molale Umfang V_c stimmt mit dem durch Messungen des Elastizitaetsmoduls erhaltenen gut ueberein. Eine Analyse frueherer Daten ueber das Quellen von Polybutadien zeigt, dass die Zahl der Querverbindungen dem Schwefelgehalt proportional ist.

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Photochemistry of Proteins. VI. pH Dependence of Quantum Yield and Ultraviolet Absorption Spectrum of Chymotrypsin[1]

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For pepsin a marked pH dependence of the quantum yield has been found at constant wave length (1). Similar behavior has now been found for chymotrypsin, trypsin (2) and trypsin inhibitor (2). The results on trypsin and soybean trypsin inhibitor will be presented elsewhere. Results for chymotrypsin are reported here along with an investigation of the effect on the quantum yield of varying various other parameters including light intensity, concentration of the irradiated solution, speed of stirring and the effect of the presence or absence of oxygen in both alkaline and acid buffers.

A study was also made of the effect of pH changes on the ultraviolet absorption spectrum of the native enzyme and of the partially denatured enzyme inactivated both in the presence and absence of oxygen. An amino acid mixture with a composition corresponding to that of chymotrypsin was also examined in acid and alkaline solutions.

EXPERIMENTAL

Details of irradiation techniques are described elsewhere (1).

Preparation of chymotrypsin. A sample of Plaut[4] chymotrypsinogen was recrystallized 5 times and converted to chymotrypsin according to the directions of Kunitz and Northrop (3). After one recrystallization the product was dried for three days in a refrigerator at 5°. The average chymotrypsin content of the preparation was 35.5%; the remainder was magnesium sulfate and water.

Activity Determinations. The concentrations of stock native enzyme solutions were determined by optical density by the method of Kunitz (4) (p. 309). For following loss in enzyme activity with irradiation, the calibration curve reported in a previous paper in this series was used (5) with casein as a substrate (4). The casein used for both investigations was from the same bottle.

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[1] This study will comprise part of the Doctoral thesis to be submitted by P. Finkelstein to the Graduate School of the Polytechnic Institute of Brooklyn.

[2] Fellow of the Monsanto Chemical Company, 1948-49.

[3] Presented at the Gordon Research Conferences, A.A.A.S., on Polymers, July 12-16, 1948.

[4] Plaut Research Laboratory, Lehn and Fink Products Corp., Bloomfield, N. J.

Irradiation as a Function of pH. Details of the equipment for the irradiation by monochromatic ultraviolet light of λ 2537 A. are given in references 1 and 5. The irradiations at various pH's were carried out in *M*/15 phosphate buffers. These buffers were made up by mixing appropriate quantities of *M*/15 disodium hydrogen phosphate, *M*/15 potassium dihydrogen phosphate, and *M*/15 phosphoric acid. For pH 10 a little 0.1 *N* sodium hydroxide was added to *M*/15 disodium hydrogen phosphate to adjust to the desired pH. The pH's were all checked with a Beckman pH meter.

The enzyme employed in determining the quantum yields was our preparation except where indicated at pH 8.89, where a salt-free sample was used[1]. The quantum yield for the two samples checked closely. The same salt-free sample was used to examine the absorption spectra because with this sample no trouble was encountered with a magnesium precipitate in the alkaline range. Since the magnesium sulfate containing sample was used to get the quantum yield at pH 8.60 and 10.02 a precipitate had to be centrifuged off before irradiation. At pH 10.02 some alkali denaturation was observed (10 to 17%), but in all cases a parallel unirradiated sample was used for the standard activity. At lower pH's no alkali denaturation was observed. At pH 7.50 a loos in activity of 6.5 to 10% was observed. This was ascribed to autolysis of the enzyme as described by Jacobsen (6) and Kunitz (7) in this pH range.

Quantum Yield as a Function of Intensity. To reduce the light intensity the distance between the ultraviolet light source and the irradiation cell was simply increased. The intensity was reduced sixfold from 1.64×10^{-5} to 2.75×10^{-6} einstein per cubic centimeter per hours (the einstein equals Nh ν where N is Avogadro's number, h is Planck's constant and ν the frequency at 2537 A.). For data see Table I.

Quantum Yield as a Function of Concentration. The initial enzyme concentration in the irradiation cell was varied from 2.04×10^{-8} to 8.16×10^{-9} moles/ml. in separate experiments and the fraction of the light absorbed from 85% to 45% without change in quantum yield. Except where indicated, however, the per cent light absorbed was between 75 and 85%. The data is in Table I. The speed of stirring in separate experiments was varied from 135 to 1000 r.p.m. with no change in quantum yield.

Quantum Yields With and Without Oxygen. Irradiation in the presence or absence of oxygen was carried out in a special quartz cell into which oxygen or nitrogen was continuously bubbled for one hour prior to the irradiation, and all during the irradiation. The gas stream was used to produce the agitation. Serious surface denaturation, due to foaming of the protein caused by the gas bubbles, was encountered and erratic results were obtained until a little n-octyl alcohol (about 0.01 ml.) was added to displace the protein from the surface layer. This completely prevented the foaming and the surface denaturation. Prior to passing the nitrogen gas into the solution the last traces of oxygen were removed by means of a gas absorption train containing Fieser's solution (8).

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[1] Worthington Biochemical Laboratory, Freehold, N. J., salt-free sample containing 86.0% protein and 14% moisture.

Table I. Quantum Yields as a Function of pH

pH	$\Phi \times 10^3$	pH	$\Phi \times 10^3$
1.72	8.47[a]	5.43	2.38[a]
3.00	4.77	6.01	2.97
3.00	5.06[a,e]	7.50	4.90[b]
3.00	4.80[a,d]	8.60	7.57[a]
4.52	2.97	8.89	7.32[c]
4.65	3.18	10.02	7.29[a]

[a] Average of two determinations.
[b] Average of three determinations.
[c] Salt-free enzyme.
[d] Light intensity reduced sixfold.
[e] Per cent light absorbed reduced to 45% and initial concentration reduced to 8.16×10^{-9} moles/ml.

RESULTS

The method employed in calculating the quantum yield in a previous paper (5) was simplified as follows (1). It has been previously shown that the light-induced denaturation of chymotrypsin is kinetically first order to beyond 80% inactivation (5). Thus:

$$E = E_0 e^{-k_I I_0 t} \tag{1}$$

where E is the concentration in moles per cubic centimeter of active enzyme at any time and E_0 the concentration at $t = 0$.

The quantum yield is defined as:

$$\Phi = \frac{\text{number of moles inactivated}}{\text{number of einsteins absorbed}} \tag{2}$$

$$\text{Number of moles inactivated} = E_0 - E = E_0(1 - e^{-k_I I_0 t}) \tag{3}$$

$$\text{Number of einsteins absorbed} = I_0 t - It = I_0 t(1 - e^{-kcd}) \tag{4}$$

by the Beer-Lambert Law, where I_0 = incident light intensity; I = transmitted light intensity, and c = concentration of total protein.

If it is assumed that reactants and products absorb alike, then the einsteins absorbed by active protein on the average is given by:

$$\text{Einsteins absorbed} = I_0 t(1 - e^{-kcd})\ \bar{E}/E_0 \tag{5}$$

where $\bar{E}$ = average concentration of enzyme in the time interval, t, of the irradiation, i.e.,

$$\bar{E} = \frac{E_0}{t}\int_0^t e^{-k_I I_0 t}\,dt \qquad (6)$$

Substituting these values into the definition for Φ we get:

$$\Phi = \frac{E_0 \ln(E_0/E)}{I_0 t(1 - e^{-kcd})} = \frac{E_0 \ln(E_0/E)}{\text{einsteins absorbed during exposure per cc.}} \qquad (7)$$

This calculation, of course, gives results identical with those calculated by the original formula. This method, however, has the advantage of simplicity and automatically corrects for the fraction of the light absorbed by the active remaining enzyme at any instant. It was observed that the per cent of light absorbed during irradiations increased, hence quantum yields were calculated from low percentages of inactivation (about 10%) wherein the approximation of equation (5) is permissable. Quantum yields were found to be reproducible to within 6% of the average. A plot of log E/E_0 vs. time of irradiation was always a straight line as far as studied, namely 65% to 85%. The quantum yields at various pH's are tabulated in Table I and are plotted in Figure 1.

From Figure 1 it is seen that the quantum yield is a minimum at the isoelectric point, pH 5.4 (9), and increases as an increasing net positive or negative charge resides in the molecule.[1]

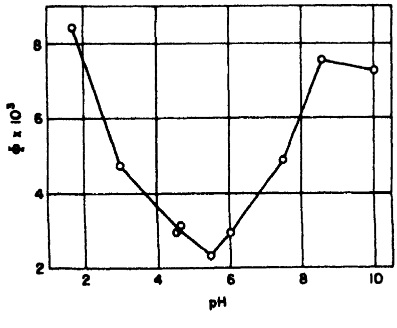

Fig. 1. Quantum yield versus pH for chymotrypsin.

Figure 2 shows the change of the absorption spectrum after irradiation at pH 3.00 in the presence of nitrogen and oxygen as compared with the unirradiated protein spectrum. The remaining activity toward casein was 77.0% and 73.5%, respectively, for the irradiated samples and the quantum yield was the same. This shows that the spectrum after irradiation under nitrogen parallels the shape of the unirradiated sample, but is displaced upward, whereas the sample irradiated in oxygen has a spectrum that dips below the unirradiated one slightly in the region of the absorption maximum. This trend is more clearly shown (Fig. 2) where inactivation was carried much further to a calculated remaining activity of 0.3%.[1]

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[1] In a more recent paper, however, Anderson and Alberty, J. Phys. and Colloid Chem., 52, 1345 (1948) have reported a widely different isoelectric point (pH. 8.1 to 8.6 depending on the ionic strength of the medium).

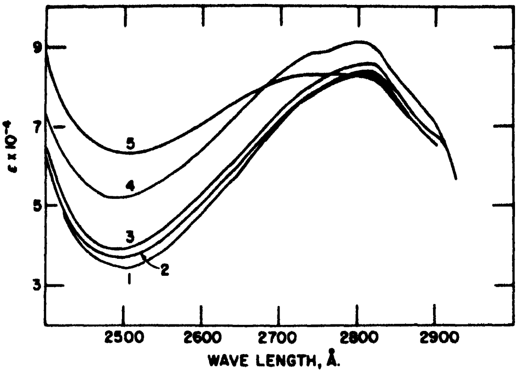

Fig. 2. Extinction versus wave length of irradiated chymotrypsin solutions, pH 3. 1, control· unirradiated; 2, irradiated under oxygen, 73.5% remaining activity; 3, irradiated under nitrogen, 77.0% remaining activity; 4, irradiated under oxygen, about 0.3% remaining activity; 5, irradiated under nitrogen, about 0.3% remaining activity.

A sample of the material irradiated under nitrogen to 77.0% remaining activity was brought to pH 10.5 to observe any change that might take place in the shape of the spectrum due to ionization of any previously bound groups such as tyrosyl hydroxyl, which could have been liberated during the irradiation (see below). No such changes were observed, i.e., the absorption spectrum was more like that in Figure 4 than the corresponding curve in Figure 5.

Similar experiments were carried out at pH 8.6 so as to leave 77.0% remaining activity under both oxygen and nitrogen in one case and a calculated remaining activity of 0.3% for another. The spectra for these samples are all shown in Figure 3. Here again it is seen that the shape of the curves for the samples having 77.0% remaining activity is hardly changed at all. Much further inactivation under nitrogen again leads to a curve parallel to the unirradiated curve but displaced upward. The prolonged irradiation in oxygen leads to a marked decrease in the region of the absorption maximum. The enzyme solutions irradiated at pH 8.60 under nitrogen and oxygen to about 0.3% remaining activity were brought to pH 12.78 and the spectra determined. Here also no definite evidence for the liberation of ionizing tyrosyl hydroxyl groups was found (see below). The quantum yield was identical under both oxygen and nitrogen.

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[1] All spectra plotted in terms of molecular extinction coefficients:

$$\log \frac{100}{\%\ \text{Transmission}} = \text{Optical density} = \epsilon Cd$$

where ϵ = the molecular extinction coefficient; C = concentration in moles/per liter; and d = depth of absorption cell, 1 cm. In the case of the amino acids mixture a molecular weight the same as that of chymotrypsin (41,000) was assumed.

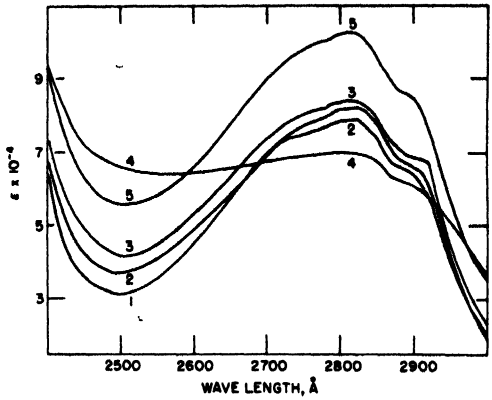

Fig. 3. Extinction versus wave length of irradiated chymotrypsin solutions, pH 8.6. 1, control: unirradiated; 2, irradiated under nitrogen, 77% remaining activity; 3, irradiated under oxygen, 77% remaining activity; 4, irradiated under nitrogen, about 0.3% activity remaining; 5, irradiated under oxygen, about 0.3% activity remaining.

DISCUSSION

It has been shown that in the native form of some proteins tyrosine hydroxyl groups are bound. This is true in egg albumin (10), in bovine serum albumin (11) and in soybean trypsin inhibitor (12) but not in insulin (10). At high alkali concentrations, e.g., pH 12, a protein exhibiting this characteristic is denatured and the specific ultraviolet absorption band of unbound tyrosine appears. Lowering of the pH to, for example, 10, does not result in the reappearance of the spectrum of the native protein, proving that this extreme alkali denaturation is not reversible.

A comparison of the spectra of an amino acid mixture, Figure 5, which contains acids in the same proportions as found in the enzyme,[1] with that of the native chymotrypsin, Figure 4, shows a very marked similarity in shape in the acid region, with the position of minima and maxima shifted somewhat toward longer wave lengths for the enzyme. Increasing the pH has a markedly different effect on the spectrum of the amino acids as compared with the spectrum of the enzyme. In the case of the amino acid mixture the molecular extinction coefficient in the region around 2400 A. increases only slightly from pH 3.00 to 9.50. At pH 10.6, however, a plateau appears and this increases somewhat as the pH is raised to 14.0. Also, the slight shoulder at about 2875 A. becomes more pronounced as the pH is raised from pH 9.5 to 10.6, but not at lower pH's. This change in absorption is attributed to the ionization of the phenolic groups of tyrosine (10,11). The absorption spectrum of tyrosine itself shows a sharp peak at about 2400 A. in the alkaline range. Also observed is a shift of the maximum from about 2740 A. to about 2940 A. and to higher molecular extinction coefficients.

Sizer and Peacock have also reported the absorption spectrum of an amino acid mixture corresponding to bovine serum albumin and found a peak around 2400 A. similar to that found for tyrosine alone.

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[1] The amino acid composition is given in reference 9, p. 26.

In the amino acid mixture corresponding to chymotrypsin, however, we find only a plateau appearing in this region of the spectrum. This is attributed to the fact that chymotrypsin has about twice as much phenylalanine, about ten times as much tryptophane and only about half as much tyrosine (13) as bovine serum albumin on a weight basis. Since these three amino acids are responsible for most of the absorption in this region of the ultraviolet any change due to the tyrosine would be relatively more difficult to pick up. Further, the molecular extinction coefficient of tryptophane is considerably higher than that of tyrosine thus obscuring changes due to tyrosine still more.

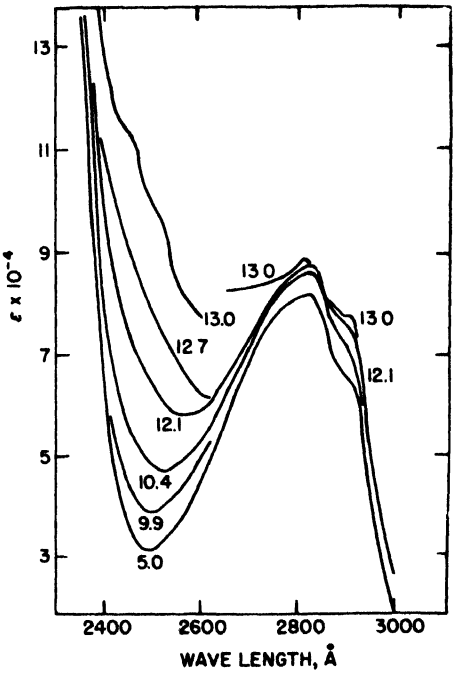

Fig. 4. Absorption spectrum of chymotrypsin at various pH (indicated by figures on curves).

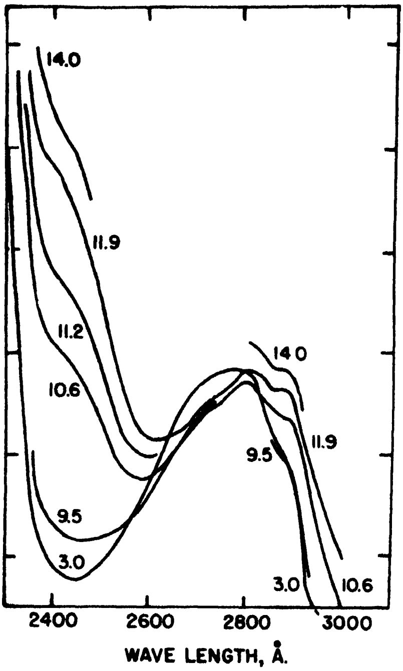

Fig. 5. Absorption spectrum of amino acid mixture at various pH (indicated by figures on curves).

Examining the shift in the absorption spectrum of the native enzyme, Figure 4, with pH we observe a shift of the minimum toward longer wave lengths and an increase in the molecular extinction coefficient. But only at pH 13.0 is there even a slight sgggestion of a plateau at 2440 A. A slight increase in the shoulder around 2900 A. is also observed at pH 13.0. Thus, it is concluded that in the native chymotrypsin the tyrosine is not free to ionize until a pH of 13 is reached. In this very alkaline solution, however, the absorption was found to be changing significantly as the spectrum was being taken due to the finite rate of denaturation-inactivation. Thus, two separate curves were taken at this alkaline pH on different solutions beginning at opposite ends of the spectrum to try to minimize the effect of alkali denaturation which was occurring quite rapidly.

An examination of the spectra of the irradiated enzyme indicates that for inactivation of about 25% the shapes of the curves are hardly altered at all. This obtains whether the irradiation takes place in nitrogen or in oxygen, in acid or in alkaline buffer. Furthermore, the quantum yield is unchanged under nitrogen or oxygen thereby indicating that the primary photochemical process leading to the loss of enzymatic activity is not a photooxidation.

When the irradiated solutions are brought to alkaline pH's, 10.5 and 12.78, no plateau appears around 2400 A. as is observed in the amino acid mixture. Therefore, it is concluded that during the inactivation large amounts of tyrosine have not become free to ionize. It is evident, however, that small amounts of phenolic ionization of tyrosine would be difficult to detect in this manner due to the relatively small amounts of tyrosine in the native protein.

Carrying the inactivation much further, down to less than 1% remaining activity, produced decided differences in the shape of the absorption spectra of solutions irradiated under nitrogen on the one hand and oxygen on the other. The irradiation under nitrogen simply shifted the entire curve to higher extinction coefficients without altering its shape. But under oxygen there appeared a much flatter peak in the region of the absorption maximum around 2800 A. Thus it seems that although the primary photochemical process leading to loss of enzymatic activity is not photooxidative, secondary processes may be, depending on the atmosphere during irradiation (14). It is interesting that Becker and Szendrö (15) have reported changes in the absorption spectrum of egg albumin after irradiation under nitrogen and oxygen; the absorption around the maximum at 2800 A. disappearing in oxygen but not in nitrogen. They also reported a general absorption increase throughout the spectrum after irradiation as we have observed in all cases. It has been shown that the characteristic absorption band common to most proteins and having its maximum around 2800 A. is predominantly due to those amino acids containing aromatic rings (16,17). It is suggested therefore that the decreased absorption on prolonged irradiation under oxygen is due to the cleavage of these rings. Arnow (18) has proposed a similar cleavage to account for decreased absorption after irradiation of egg albumin with alpha particles.

The lack of appreciable ionization of tyrosyl hydroxyl below pH 10-11 led us to look for an increase in quantum yield as the pH is increased from pH 7 to pH 10. It seemed possible that near pH 10 the molecule would be under a strain from electrostatic repulsion of ionized groups (19) and absorbed energy from irradiation would be more efficient in inducing denaturation-inactivation. It is true that the quantum yields are higher as the pH is raised; however, the quantum yield also increases as the pH is lowered from about pH 5.4. Our over-all explanation thus does not need to emphasize the role of tyrosine since the binding of tyrosine could hardly be significant for the rise in quantum yield at low pH's. The explanation offered here is similar to that offered for a similar phenomenon with pepsin (1), with the difference that, unlike pepsin, chymotrypsin has a more nearly equal number of acidic and basic residues per molecule. At the isoelectric point the net charge on the molecule is zero. On either side of the isoelectric point a net charge is extant. Let us assume that the peptide chain(s) of the chymotrypsin molecule are folded into a unique configuration which is stabilized by salt and hydrogen bonds (20). We may postulate that on absorption of an active quantum a split occurs at one of the weaker linkages (21), e.g., -SS- or -CONH-. The free ends of linkage can react with the solvent, leading to denaturation (22), or recombine. The probability for recombination is high because of what we choose to call an internal Franck-Rabinowitch effect (23,24). This effect is, we predict, that a high probability for recombination of radicals exists because the chains are held in a network within the molecule (20). On either side of the isoelectric point a net repulsion will exist within the molecule and this will result in a decreased tendency for recombination of the free ends of the linkage; the net result is an increase in quantum yield on either side of the isoelectric point. (See, however, footnote on page 576).

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Synopsis

The quantum yield of inactivation of chymotrypsin was found to be independent of variations in conditions of irradiation including light intensity, concentration of the irradiated solution, rate of stirring and the presence or absence of oxygen. The quantum yield for inactivation is at a minimum at the isoelectric point (pH 5.4). An explanation is offered for the variation of the quantum yield with pH in terms of an internal Franck-Rabinowitch mechanism. The absorption spectra of the enzyme was also studied as a function of pH, as was that of an amino acid mixture whose composition corresponded to that of chymotrypsin. Evidence is presented for the existence of bound, un-ionizing tyrosine in the native enzyme and of unbound tyrosine in alkali-denatured enzyme. The significance of changes in the absorption spectra accompanying irradiation is discussed.

Résumé

Le rendement quantique de l'inactivation de la chymotrypsine est indépendant des variations des conditions d'irradiations, telles l'intensité lumineuse, la concentration des solutions irradiées, la vitesse d'agitation de la solution et la présence ou l'absence d'oxygène. Le rendement quantique pour l'inactivation atteint un minimum au point isoélectrique (pH 5.4). Une explication pour les variations du pH est suggérée dans le sens d'un mécanisme interne Franck-Rabinowitch. Le spectre d'absorption de l'enzyme, ainsi que du mélange d'acides amines, qui correspond à la composition de la chymotrypsine, a été également suivi en fonction du pH. Durant la dénaturation en milieu alcalin, l'existence de tyrosine non-ionisée et liée a été mise en evidence. Les auteurs ont également essayé d'interpréter les modifications du spectre d'absorption au cours de l'irradiation.

Zusammenfassung

Die Quantumausbeute der Inaktivierung von Chymotrypsin ist unabhaengig von den Bedingungen der Bestrahlung, wie zum Beispiel Lichtstaerke, Konzentration der bestrahlten Loesung, Ruehrungsgeschwindigkeit und Gegenwert oder Abwesenheit von Sauerstoff. Die Quantenausbeute der Inaktivierung ist am Niedrigsten am isoelektrischen Punkte (pH:5.4). Eine Erklaerung der Veraenderung der Quantumausbeute mit pH wird vorgeschlagen im Sinne eines inneren Frank-Rabinowitsch'schen Mechanismus. Die Absorptions-Spektren des Enzymes sowie einer Mischung von Aminosaeuren deren Zusammensetzung derjenigen von Chymotrypsin entsprach, wurden auch als eine Funktion des pH studiert. Evidenz fuer das Vorkommen von gebundenem unionisierten Tyrosin im Rohenzym und in durch Alkalien denaturierten Enzymen wird geboten. Die Bedeutung der Veraenderungen in den Absorptionsspektren waehrend der Bestrahlung wird eroertert.

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Emulsion Polymerization of 2-Alkyl-1,3-butadienes[1]

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Since three new 2-alkyl-1,3-butadienes have become available (1), it has been of interest to study their polymerization and their copolymerization with styrene and with butadiene in an emulsion system similar to the GR-S system (2).

It has been found that the 2-alkylbutadienes prepared from the corresponding 2-alkyl-3-acetoxy-1-butenes (1b) polymerize somewhat more slowly than does pure isoprene in the GR-S system. In twenty-four hours the respective conversions for the ethyl, isopropyl, and n-amyl derivatives are 87.5%, 72.5%, and 67.0%. The intrinsic viscosities of the polymers are lower than for polyisoprene prepared in the same system, which shows that they need less modifier to give soluble polymers.

The polymers of the 2-alkylbutadienes show the expected amount of unsaturation by iodine chloride titration, and the ratios of 1,2 to 1,4 units in the polymers are 15 to 85 (±2), which is a very close check with the ratio reported for isoprene (3).[3]

In addition to the 2-alkylbutadiene monomer synthesized in this Laboratory, polymerization of a sample of 2-ethyl-1,3-butadiene prepared by the Carbide and Carbon Chemicals Corporation[4] has been carried out. This material polymerized more slowly than the 2-ethyl-1,3-butadiene synthesized in this Laboratory, requiring ninety-six hours to reach 70-75% conversion. The slowness of polymerization may have been due to traces of inhibiting materials not removed by the particular purification procedure employed in this Laboratory before polymerization. Our synthetic material differed considerably in refractive index from the Carbide and Carbon Chemicals Corporation sample.

Using data in Table I an approximate α-value (4) for each of the new dienes with respect to styrene at 75-80% conversion has been calculated. The value for similar styrene-butadiene polymerization is 0.61 (5). 2-Ethylbutadiene has an α-value of 1.1, 2-isopropylbuta-

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[3] We are indebted to Drs. I. M. Kolthoff and T. S. Lee for these analytical figures and for permission to use them in this communication.

[4] The authors are indebted to Mr. L. C. Shriver for the gift of this sample of 2-ethyl-1,3-butadiene.

TABLE I. Polymerization of 2-Alkylbutadienes

Run	Monomer(s)	Modifier, g./100 g. monomer	Time, hr.	Conversion, %	Static solubility, %	Intrinsic viscosity
1	Butadiene	0.50	15	77.5	100	2.38
2	"	0.75	19	82	100	1.68
3	"	1.00	19	87	100	1.20
4	Isoprene	0.10	17	71	Gel	-
5	"	0.10	17	70	Gel	-
6	"	0.30	17	73.5	100	1.00
7	"	0.30	17	73.5	100	1.15
8	Isoprene (75), styrene (25)	0.15	15	71.5	100	0.44
9	2-Ethyl-1,3-butadiene	0.10	25	87.5	100	1.16
10	"	0.10	25	91	100	0.73
11	"	0.20	24	85	100	0.89
12	"	0.20	24	82	100	0.87
13	2-Ethyl-1,3-butadiene*	0.10	24	43	100	0.73
14	"	0.10	24	38	100	0.71
15	"	0.10	72	70	100	1.37
16	"	0.10	72	73	100	1.32
17	"	0.10	96	80	100	1.56
18	"	0.10	96	75	100	1.39
19	"	0.10	96	70	100	1.91
20	"	0.10	97	77	97	1.90
21	2-Ethyl-1,3-butadiene*(5), butadiene (95)	0.75	19	75	100	1.72
22	"	0.75	19	75	100	1.16
23	"	0.75	19	75	98	1.45
24	"	1.00	19	73	100	0.86
25	"	1.00	19	74	100	1.04
26	2-Ethyl-1,3-butadiene (75), styrene (25)	0.20	20	85	100	1.50
27	"	0.20	20	85	100	1.42
28	"	0.30	20	85	100	1.24
29	"	0.30	20	90	100	1.04
30	2-Isopropyl-1,3-butadiene	0.01**	24	67.5	100	1.27
31	"	0.01**	24	65	100	1.67
32	"	0.10	26	75	100	1.67
33	"	0.10	26	70	100	1.74
34	"	0.10	26	70	100	1.42
35	2-Isopropyl-1,3-butadiene (5), butadiene (95)	0.50	19	73	99	2.00
36	"	0.50	19	72	100	1.80
37	"	0.75	19	70	99	1.05
38	"	0.75	19	72	98	1.21

TABLE I (continued)

Run	Monomer (s)	Modifier, g./100 g. monomer	Time, hr.	Conversion, %	Static solubility, %	Intrinsic viscosity
39	2-Isopropyl-1,3, butadiene (75), styrene (25)	0.01**	24	92.5	100	1.78
40	"	0.01**	24	92.5	100	1.85
41	"	0.20	20	85	100	1.79
42	"	0.20	20	87.5	100	1.82
43	"	0.30	20	87.5	100	1.61
44	"	0.30	20	90	100	1.57
45	2-n-Amyl-1,3-butadiene	0.05	24	50	98	1.76
46	"	0.05	40	64	98	1.58
47	"	0.05	48	80	95	2.33
48	"	0.10	24	67	100	0.88
49	"	0.10	24	67	100	0.76
50	"	0.10	24	50	97	1.24
51	"	0.10	40	64	98	1.41
52	"	0.10	48	80	97	1.79
53	"	0.10	48	81	100	1.69
54	"	0.20	24	53	95	0.79
55	2-n-Amyl-1,3-Butadiene (5), butadiene (95)	0.50	19	71	100	2.19
56	"	0.50	19	71	100	1.95
57	"	0.75	19	74	100	1.28
58	"	0.75	19	77	98	0.69
59	"	0.75	19	72	100	1.23
60	"	0.75	19	75	100	1.24
61	"	1.00	19	66	97	0.44
62	"	1.00	19	73	100	0.41
63	2-n-Amyl-1,3-butadiene (10), butadiene (90)	0.75	19	75	100	1.47
64	2-n-Amyl-1,3-butadiene (75), styrene (25)	0.10	21	70	100	1.25
65	"	0.10	21	76	100	0.92
66	"	0.10	39	76	100	1.43
67	"	0.20	39	74	100	1.07
68	"	0.45	24	53	95	0.79
69	"	0.45	24	60	99	0.81

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*Monomer obtained from the Carbide and Carbon Chemical Corporation. The authors are indebted to Mr. L.C. Shriver for the gift of this sample of 2-ethyl-1,3-butadiene.

**Cetyl mercaptan used instead of O.E.I. as a modifier.

diene of 1.8, and 2-n-amylbutadiene of 1.4. These values are not based on sufficient data to be regarded as more than tentative, but they do indicate that the rate of entry of the substituted diene into the styrene copolymer is somewhat slower than that of butadiene in the styrene copolymer.

EXPERIMENTAL

Monomers

With the exception of the sample of 2-ethyl-1,3-butadiene obtained as a gift from the Carbide and Carbon Chemicals Corporation, the monomers, 2-ethyl-, 2-isopropyl-, and 2-n-amyl-1,3-butadiene, were synthesized in this Laboratory according to the procedure of Marvel and Williams (1b) via the 2-alkyl-3-acetoxy-1-butenes. The physical constants of the monomers were as follows: 2-ethyl-1,3-butadiene (Illinois), b.p. 66°C., $n^{20}D$, 1.4325; 2-ethyl-1,3-butadiene (Carbide and Carbon Chemicals Corporation), b.p. 65.6-66.5°C., $n^{20}D$, 1.4255; 2-isopropyl-1,3-butadiene, b.p. 85°C. (738 mm.), $n^{20}D$, 1.4338; 2-n-amyl-1,3-butadiene, b.p. 140-142°C., 72-74°C. (69 mm.), $n^{20}D$, 1.4452. Before polymerization all monomers were purified to remove inhibiting substances. A given volume of monomer was washed twice with equal volumes of 20% aqueous sodium hydroxide, washed twice with water, dried over anhydrous magnesium sulfate, and distilled through a 15-cm. Vigreux-type column. The 2-n-amyl derivative was distilled at a pressure of 65 mm., the others at atmospheric pressure.

Polymerization

The emulsion polymerization of the 2-alkyl-1,3-butadienes alone and with styrene or with butadiene was carried out using a modified form of the GR-S recipe, as follows in parts by weight:

Monomer(s)	100.0
Soap (Procter and Gamble silica-free flakes)	5.0
Water	180.0
Potassium persulfate	0.30
O.E.I. (a mixture of mercaptans supplied by United States Rubber Company)	Variable (see Table I)

In a few instances cetyl mercaptan was substituted for O E.I. in the recipe, as indicated in Table I.

The polymerizations were carried out in 2- or 4-ounce screw-cap bottles whose caps were fitted with rubber disk gaskets lined with heavy tin foil. The soap was dissolved in 170 parts of warm water and charged into the bottle. After the soap solution had been allowed to cool and gel, 10 parts of freshly prepared 3% potassium persulfate solution was added, and then the monomer (s), containing the proper proportion of modifier (O.E.I. or cetyl mercaptan), was added. The amount of modifier used (see Table I) was varied in order to produce soluble polymers having intrinsic viscosities greater than 1.0 in the range of 75-85% conversion. The bottles were swept out with a moderate stream of nitrogen for one minute and then capped. The bottles were shaken vigorously to mix the ingredients and then were rotated end-over-end for the specified time (see Table I) in a bath at 50 ± 1°C. In those instances in which butadiene was one of the monomers, butadiene of the special purity grade supplied by the Phillips Petroleum Company was passed over sodium hydroxide pellets and through a 50-cm. Vigreux column and was condensed in a Dry Ice-acetone trap. The monomer other than butadiene, containing the modifier, was added to the bottle in the usual sequence of operations, the bottle and contents were chilled in ice water, slightly more than the desired amount of butadiene was poured into the weighed bottle, and the excess was allowed to boil off to remove air before the bottle was capped. From this point the polymerization proceeded as before.

The latex was mixed with 25 parts of a 3% suspension of phenyl-β-naphthylamine in soap solution and was coagulated with a saturated sodium chloride solution containing 2.3% of concentrated sulfuric acid. The polymer was washed carefully with water, shredded, and dried eighteen to twenty-four hours in a circulating air oven at 60-70°C. The polymers containing styrene and/or 2-n-amyl-1,3-butadiene were dried twenty-four hours in a vacuum desiccator at 0.1 mm. in addition to the oven drying. In calculating conversion, the residual fatty acid and antioxidant were taken into account. It was assumed, perhaps without justification, that the unpolymerized styrene and 2-n-amyl-1,3-butadiene would be removed by the dryings used for the polymers prepared from those monomers.

Intrinsic Viscosities and Static Solubilities

The intrinsic viscosities and static solubilities of the polymers and copolymers were determined by the procedure described by Frank, Adams, Blegen, Deanin, and Smith (6). The values are given in Table I.

TABLE II. Per Cent Styrene Content of the Copolymers of 2-Alkyl-1,3-butadienes with Styrene

	Per Cent Styrene	
Diene	Iodine monochloride method	Ultraviolet absorption method
2-Ethyl-1,3-butadiene	22 ± 2	25.3
2-Isopropyl-1,3-butadiene	-	27.5
2-n-Amyl-1,3-butadiene	21.4 ± 2	27.6

Analysis

For styrene, combustion, and 1,4-addition analyses the polymer samples were purified by dissolving 0.2-0.5 g. of polymer in the smallest possible amount of dry benzene and then reprecipitating the polymer by pouring the benzene solution into four to five times the volume of methanol with rapid stirring. After three such precipitations the polymer samples were dried twenty-four hours in a vacuum desiccator at 0.1 mm. and room temperature.

Samples of the copolymers of the 2-alkyl-1,3-butadienes with styrene were analyzed by ultraviolet spectroscopy[1] for styrene content. The analyses were carried out using chloroform solutions of the copolymers. In addition two of the copolymers were examined by Professor I. M. Kolthoff[2] for styrene content using the iodine monochloride technique. The results of the analyses are given in Table II. The lack of agreement between the iodine monochloride and ultraviolet absorption methods can possibly be explained by the fact that the iodine monochloride method has been shown to give unreliable results with some unsaturated molecules containing ethylenic bonds of the type $R_1R_2C=CHR_3$ where R represents an alkyl group.

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[1] We are indebted to Mrs. Dorothy D. Brantley for these analyses by ultraviolet spectroscopy.

[2] We are indebted to Drs. I. M. Kolthoff and T. S. Lee for these analytical figures and for permission to use them in this communication.

The combustion analyses[1] of the polymers and copolymers are given in Table III.

TABLE III. Combustion Analyses of Polymers

Polymer	Calculated Carbon	Calculated Hydrogen	Found Carbon	Found Hydrogen
Poly-2-ethyl-1,3-butadiene......	87.73	12.27	88.81* 87.67*	11.98* 12.29*
Poly-2-isopropyl-1,3-butadiene..	87.42	12.58	87.29	12.35
Poly-2-n-amyl-1,3-butadiene.....	87.01	12.99	86.89	12.78
Copolymer of 2-ethylbutadiene (75) and styrene (25).........	89.01	10.99	88.90	11.12
Copolymer of 2-isopropylbutadiene (75) and styrene (25)...	88.97	11.03	88.38	11.16
Copolymer of 2-n-amylbutadiene (75) and styrene (25).........	88.56	11.44	87.91	11.58
Copolymer of butadiene (95) and 2-ethyl-1,3-butadiene (5).....................	88.59	11.41	88.10	11.08
Copolymer of butadiene (95) and 2-isopropyl-1,3-butadiene (5).....................	88.57	11.43	88.17	11.07
Copolymer of butadiene (95) and 2-n-amyl-1,3-butadiene (5).....................	88.55	11.45	88.41	11.21

* The first values given are for polymer prepared from Illinois monomer and the second values given are for polymer prepared from Carbide and Carbon Chemicals Corporation monomer.

Samples of the polymers and the copolymers with styrene were analyzed by Professor I. M. Kolthoff[2] for total unsaturation (iodine monochloride method) and 1,4 units (perbenzoic acid titration). The results of these analyses are given in Table IV.

EVALUATION OF POLYMERS

Samples of typical homopolymers and copolymers with butadiene prepared from the 2-alkylbutadienes were sent to the Government

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[1] The microanalyses reported in this report were done by the Clark Microanalytical Laboratories, Urbana, Illinois.

[2] We are indebted to Drs. I. M. Kolthoff and T. S. Lee for these analytical figures and for permission to use them in this communication.

Laboratories, University of Akron, for evaluation.[1] The 2-alkylbutadiene polymers and their copolymers with butadiene (95 parts butadiene, 5 parts 2-alkylbutadiene) were compared with polyisoprene, polybutadiene and standard GR-S in the standard stress-strain tests and in the Gehman low-temperature test (7).

The standard GR-S test recipe, as shown below, was used for compounding the polymers.

Ingredients	Parts
Polymer..	100.
EPC carbon black.........	40.
Zinc oxide..............	5.
Sulfur..................	2.
Altax...................	1.75

In general 20 g. of raw polymer was used in preparing the compound. Cured samples were heated to 292°F. for ninety minutes. In some instances 20 g. of polymer from a single polymerization run was not available, and in these instances the required 20 g. was obtained by mixing two polymers of nearly identical conversions, solubilities, and intrinsic viscosities.

TABLE IV. Per Cent Unsaturation and 1,4 Addition

Polymer	Per Cent unsaturation	Per Cent 1,4 addition	Per Cent 1,2 and 3,4 addition
Poly-2-ethyl-1,3 butadiene	100.3 ± 2	85 ± 2	15 ± 2
Poly-2-isopropyl-1,3-butadiene	107*	85 ± 2	15 ± 5
Poly-2-n-amyl-1,3-butadiene	99.5 ± 2	85 ± 2	15 ± 2
Copolymer of 2-ethyl-1,3-butadiene (75) with styrene (25)	78.0 ± 2	85 ± 2	15 ± 2
Copolymer of 2-isopropyl-1,3-butadiene (75) with styrene (25)	81**	82 ± 5	18 ± 5
Copolymer of 2-n-amyl-1,3-butadiene (75) with styrene (25)	79.4 ± 2	85 ± 2	15 ± 2

*The value 100 was used in the calculation of per cent 1,4 addition.

**The value 79 was used in the calculation of per cent 1,4 addition.

The stress-strain data (measured at 77°F.) are given in Table V. The experimental data from the Gehman low-temperature test are expressed graphically in Figures 1,2, and 3, in which the angular degrees of twist (measured after ten seconds) are plotted against temperature.

[1] We are indebted to Mr. J. W. Schade and Mr. W. K. Taft of the Government Laboratories, University of Akron, for their cooperation in evaluating these polymers and for their permission to include the data in this communication.

TABLE V. Stress-Strain Data at 77° F.

Monomer(s) from which polymer was prepared	Run*	Min. cured at 292° F.	300% modulus, p.s.i.	Tensile strength, p.s.i.	Elongation, %	Set, %
Butadiene	-	30	670	1460	470	-
		60	950	1540	390	-
		90	1020	1930	420	-
		150	1090	1480	360	-
Isoprene	-	30	530**	800	280	-
		60	720**	770	230	-
		90	630**	840	250	-
		150	630**	940	260	-
2-Ethylbutadiene	20	30	840	1170	400	-
		60	1080	1080	360	-
		90	1110	1110	330	-
		150	920	1040	270	-
2-Isopropylbutadiene	34	30	340	1210	850	42
		60	440	1690	800	46
		90	520	1570	710	35
		150	430	1520	760	33
2-n-Amylbutadiene	53	30	420	1520	740	54
		60	490	1410	650	40
		90	430	1300	640	32
		150	350	1250	720	31
Butadiene (75), styrene (25) (standard GR-S)	-	30	730	3050	710	19
		30	680	2430	680	18
		60	1290	3680	570	14
		60	1260	3520	570	12
		90	1520	3310	480	9
		90	1500	3340	490	8
		150	1860	3120	410	5
		150	1900	2970	400	6
Butadiene (95), 2-ethylbutadiene (5)	22-23	30	790	1330	460	-
		60	1220	1550	360	-
		90	1270	1620	330	-
		150	-	1390	270	-
Butadiene (95), 2-isopropylbutadiene (5)	35-36	30	930	1940	480	8
		60	1500	2280	390	5
		90	1610	2640	370	4
		150	2020	2100	310	3
Butadiene (95), 2-isopropylbutadiene (5)	37-38	30	490	1250	560	13
		60	980	2010	510	11
		90	1180	1980	450	8
		150	1260	1820	390	6

TABLE V (continued)

Monomer(s) from which polymer was prepared	Run*	Min. cured at 292° F.	300% modulus, p.s.i.	Tensile strength, p.s.i.	Elongation, %	Set, %
Butadiene (95), 2-n-amylbutadiene (5)	55-56	30	1530	1570	310	6
		60	-	1750	250	4
		90	-	1860	240	3
		150	-	1740	230	3
	59-60	30	590	1320	520	9
		60	1030	2070	480	9
		90	1120	2020	440	6
		150	1280	1940	390	5
Butadiene (90), 2-n-amylbutadiene (10)	63	30	770	1730	500	10
		60	1490	2010	390	5
		90	1470	2150	370	6
		150	-	1620	280	3

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*The absence of a run number indicates that the polymer was preppared by the evaluators in their laboratory for the study under conditions similar to those used in the polymerizations described in this communication. Where two run numbers are given, samples from two runs were combined to form a 20-g. sample, 15 g. from the first run indicated and 5 g. from the second.

**Ultimate elongations were all less than 300%; consequently, moduli were measured at a lower elongation, 200%.

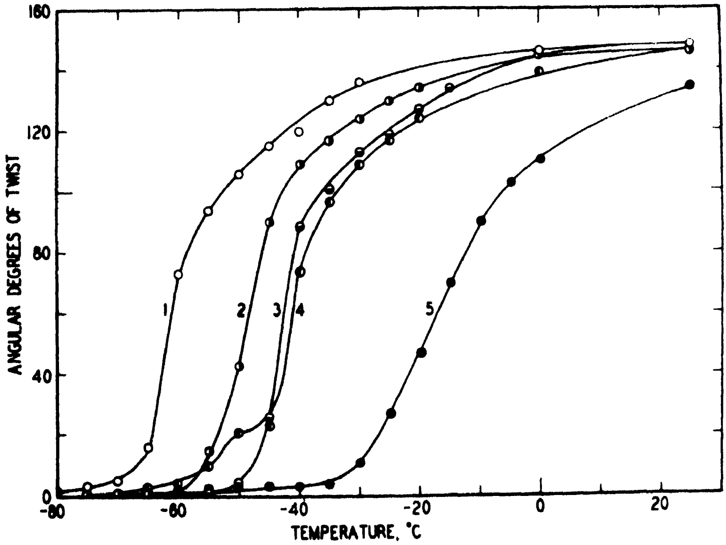

Fig. 1. Gehman low-temperature test data: (1) polybutadiene; (2) poly-2-ethylbutadiene (run 20); (3) polyisoprene; (4) poly-2-n-amylbutadiene (run 53); (5) poly-2-isopropylbutadiene (run 34).

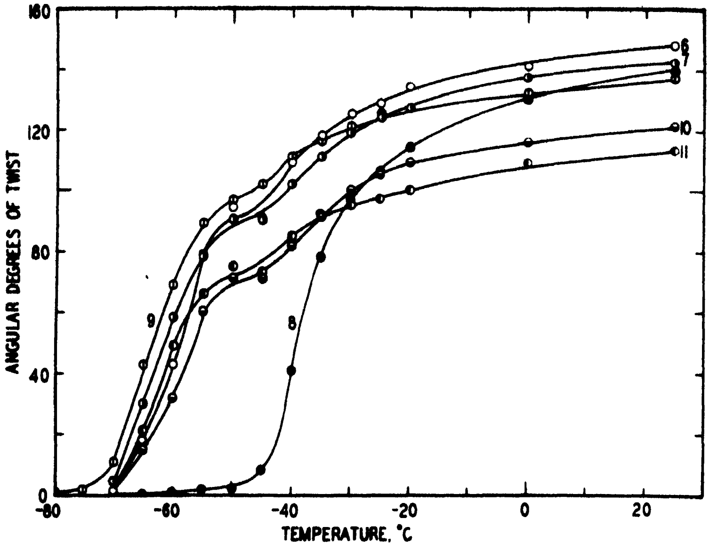

Fig. 2. Gehman low-temperature test data: (6) copolymer of 95/5 butadiene/2-isopropylbutadiene (runs 37-38); (7) copolymer of 95/5 butadiene/2-n-amylbutadiene (runs 59-60); (8) GR-S; (9) copolymer of 95/5 butadiene/2-ethylbutadiene (runs 22-23); (10) copolymer of 95/5 butadiene/2-isopropylbutadiene (runs 35-36); (11) copolymer of 95/5 butadiene/2-n-amylbutadiene (runs 55-56).

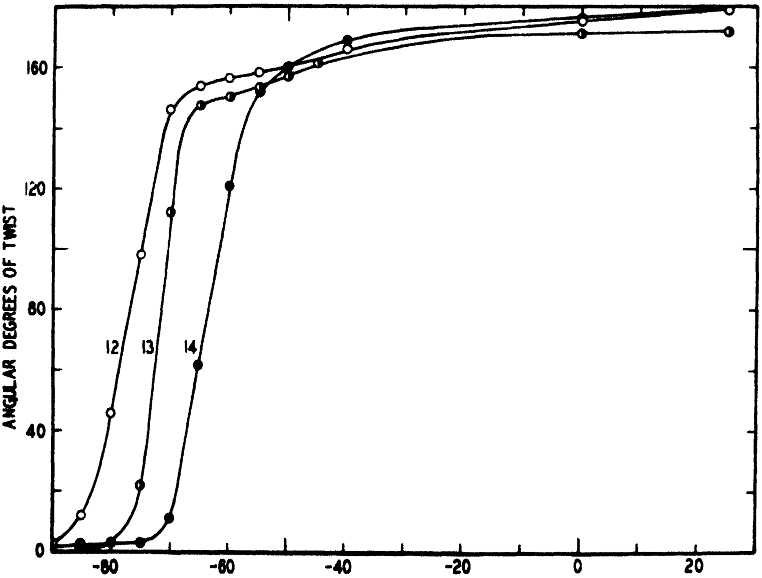

Fig. 3. Gehman low-temperature test data: (12) copolymer of 95/5 butadiene/2-ethylbutadiene (runs 22-23, uncured); (13) polybutadiene (uncured); (14) poly-2-ethylbutadiene (run 20. uncured).

TABLE VI. Results of Gehman Low Temperature Test

Monomer(s) from which polymer was prepared*	Run**	Curve	Temperature, °C.				
			T_2	T_5	T_{10}	T_{100}	Freezing point
Butadiene (raw)	-	13	-38	-62	-68.5	-74.5	-76.5
2-Ethylbutadiene (raw)	20	14	14	- 5	-38	-60.5	-70.5
Butadiene (95), 2-ethylbutadiene (5) (raw)	22-23	12	18	0	-23	-73.5	-85
Butadiene	-	1	-37.5	-57.5	-61.5	-67.5	-66.5
		***	-40	-60	-65	-74	-74
Isoprene	-	3	-21	-38	-42	-48	-48.5
2-Ethylbutadiene	20	2	-31	-46	-50	-57	-57
2-Isopropylbutadiene	34	5	- 3	-17	-23	-34	-32.5
2-n-Amylbutadiene	53	4	-21	-38.5	-43.5	-56.5	-54.5
Butadiene (75), styrene (25), (standard GR-S)	-	8	-20.5	-36	-39	-46	-46
Butadiene (95), 2-ethylbutadiene (5)	22-23	9	-40	-59.5	-63	-71	-72
Butadiene (95), 2-isopropylbutadiene (5)	35-36	10	-35.5	-53	-60	-69	-70
	37-38	6	-28	-49	-57	-67	-68.5
Butadiene (95), 2-n-amylbutadiene (5)	55-56	11	-32.5	-55	-61.5	-69.5	-71
	59-60	7	-44	-60.5	-64	-69	-69
Butadiene (90), 2-n-amylbutadiene (10)	63	****	-35	-55.5	-61	-70.5	-68.5

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*All samples except the first three in the table were cured 90 minutes at 292° F. The first three samples listed were tested uncured,

**The absence of a run number indicates that the polymer was prepared by the evaluators in their laboratory for the study under conditions similar to those used in the polymerizations described in this report. Where two run numbers are given, samples from two runs were combined to form a 20-g. sample, 15 g. from the first run indicated and 5 g. from the second.

***Average values for a large number of polybutadiene samples.

****The curve for this polymer is not given. The difference between this curve and curve 11 is well within the range of experimental error.

As determined by the Gehman method, the low temperature properties of the 2-ethylbutadiene and 2-n-amylbutadiene polymers appear to be similar and slightly better than those of standard GR-S and polyisoprene, but definitely poorer than those of polybutadiene. The 2-isopropylbutadiene polymer was inferior in this respect. All of the 95/5 butadiene/2-alkylbutadiene copolymers exhibited low temperature properties comparable to those of polybutadiene.

In Table VI are tabulated the values, T_2, T_5, T_{10}, and T_{100} (i.e., the temperatures at which the relative moduli are 2, 5, 10, and 100, respectively), and the freezing points obtained from the curves in Figures 1 through 3.

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Synopsis

The polymers of 2-ethyl-, 2-isopropyl-, and 2-n-amyl-1,3-butadiene alone, and their copolymers with styrene and with butadiene have been prepared and characterized. These monomers give the same ratio of 1,2 to 1,4 addition as has been noted for isoprene. Much less mercaptan must be used with these monomers than is required for butadiene to give soluble polymers. All these monomers copolymerize with styrene readily but have higher Wall α values than butadiene. The stress-strain properties and Gehman low-temperature properties of all of the new polymers have been determined by the Government Laboratories, University of Akron, and are included in this report. There appear to be no unusual properties to be noted.

Résumé

Les polymères du 2-ethyl-, 2-isopropyl-, et 2-n-amyl-1,3-butadiène ont été preparés et caractérisés, ainsi que leurs copolymères avec le styrène et avec le butadiène. Ces monomères donnent le même rapport d'addition 1,2 à 1,4 que indiqué précédemment pour l'isoprène. L'obtention de polymères solubles dans le cas de ces polymères nécessite moins de mercaptan, que dans le cas du butadiène. Tous ces monomères copolymérisent facilement avec le

styrène, mais avec des valeurs α de Wall plus élevées que le butadiène. Les propriétés tension-élongation et les propriétés de Gehman à basse température de tous ces nouveaux polymères ont été déterminés par les laboratoires du gouvernement, à l'université d'Akron; ils sont consignés dans ce rapport. Il semble ne pas y avoir de propriétés autres, que les propriétés habituelles.

Zusammenfassung

Die Polymerisate von 2-Aethyl-, 2-Isopropyl-, und 2-n-Amyl-1,3-Butadien sowie ihre Mischpolymerisate mit Styrol und mit Butadien wurden hergestellt und bewertet. Diese Monomere geben das selbe Verhaeltnis von 1,2 und 1,4 Addierung das fuer Isopren beobachtet wurde. Viel weniger Merkaptan muss mit diesen Monomeren benuetzt werden, um loesliche Polymerisate zu erhalten, als dies mit Butadien der Fall ist. Alle diese Monomere bilden leicht Mischpolymerisate mit Styrol, haben aber hoehere α -Werte als Butadien. Die Zug-Spannung Eigenschaften und die Gehman-Eigenschaften bei niedrigen Temperaturen aller neuen Polymerisate wurden in den Regierungslaboratorien an der Universitaet von Akron festgestellt und sind in dieser Abhandlung enthalten. Keine bemerkenswerten Eigenschaften scheinen vorzukommen.

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Copolymerization. VII. Relative Rates of Addition of Various Monomers in Copolymerization

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INTRODUCTION

Within the last four years the theory of vinyl copolymerization has progressed to the point at which quantitative predictions concerning monomer reactivity in copolymerizations can be made. Alfrey and Price (1) proposed that monomer reactivity in copolymerization is related to two constants Q and e which are unique for each monomer. The validity of this relationship is now tell established and has been checked by these laboratories (2) and by Price (3) using the published data of numerous authors. Copolymerization data have been obtained in great quantity, a partial list of which is given (4).

The prior literature, however, with the exception of data on itaconic acid (5) is devoid of copolymerization studies on unsaturated acids. The purpose of this paper is to present data we have obtained on copolymerizations involving acrylic acid, methacrylic acid, and crotonic acid as well as other monomers. The systems studied include styrene-methacrylic acid, styrene-acrylic acid, vinylidene chloride-crotonic acid, and vinyl acetate-crotonic acid. The reactivity ratios, r_1 and r_2, for these copolymerizations were obtained in the conventional way by allowing polymerizations to proceed to conversions of less than 4%, isolating and purifying the initial copolymer formed, and analyzing for carbon and hydrogen in the case of styrene-methacrylic acid and styrene-acrylic acid copolymerizations, for chlorine in the case of vinylidene chloride-crotonic acid copolymerization, and for acid numbers in the case of vinyl acetate-crotonic acid copolymerization. Other copolymer systems studied are acrylonitrile-vinyl 2-ethylhexoate, acrylonitrile-vinyl formate, acrylonitrile-vinyl benzoate, acrylonitrile-α-acetoxystyrene, acrylonitrile-allyl chloride, vinylidene chloride-vinyl benzoate, vinylidene chloride-methyl isopropenyl ketone, vinyl chloride-vinyl isobutyl ether, and styrene-citraconic anhydride.

RESULTS AND DISCUSSION

All of the experimental data obtained are consistent with and lend further support to the general scheme of monomer reactivity in copolymerization as proposed by Alfrey and Price. The experimental results and analytical data are summarized in Table I-XIII.

The r_1 and r_2 monomer reactivity ratios for these systems were determined by choosing values which gave the best curve fit on

TABLE I. Styrene-Methacrylic Acid Copolymerizations. Mass Polymerization at 60°, 0.1% Bz_2O_2

Monomer, mole % styrene	Conversion, wt. %	Analyses: Carbon I	Carbon II	Hydrogen I	Hydrogen II	Copolymer, mole % styrene
95.0	< 3	85.67	85.53	7.44	7.54	78.4
75.0	< 3	76.97	77.01	7.76	7.69	54.2
50.0	< 3	72.23	72.33	7.66	7.73	39.7
25.0	< 3	66.60	66.35	7.30	7.29	25.6
5.0	< 3	59.24	59.03	7.28	7.05	8.4

TABLE II. Styrene-Acrylic Acid Copolymerizations. Mass Polymerization at 60°, 0.1% Bz_2O_2

Monomer, mole % styrene	Time at polymerization temp., hrs.	Conversion wt. %	Analyses: Carbon I	Carbon II	Hydrogen I	Hydrogen II	Copolymer, mole % styrene
93.0	Very short	< 3	86.40	86.44	7.54	7.56	81.6
50.5	Very short	< 3	75.68	75.72	7.06	7.11	52.3
27.1	24 hrs. at 23°	< 3	72.52	72.82	7.36	7.16	45.4
7.7	Same as above		63.60	63.60	6.71	6.58	26.5

TABLE III. Vinylidene Chloride - Crotonic Acid Copolymerizations. Dioxane Solution Polymerization at 60°, 0.1% Bz_2O_2

Monomer, mole % vinylidene chloride	Time at polymerization temp., hrs.	Conversion wt. %	Chlorine I	Chlorine II	Copolymer, mole % vinylidene chloride
88.9	--	< 3	72.65	72.66	99.3
42.2	3.0	< 3	70.81	71.17	96.5
18.25	2.0	< 3	67.62	67.75	91.6

TABLE IV. Vinyl Acetate - Crotonic Acid Copolymerizations. Mass Polymerization at 68°, 0.05% Bz_2O_2

Monomer, Mole % vinyl acetate	Time at polymerization temp., hrs.	Conversion, wt. %	Acid No.[a] I	Acid No.[a] II	Copolymer, mole % vinyl acetate
90	16.5	5.0	134.9	136.3	79.2
80	16.5	1.6	188.9	196.9	70.4
60	16.5	1.6	276.5	274.5	57.8
40	16.5	2.0	297.9	300.9	54.0

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[a] Milligrams of KOH to neutralize 1 gram of sample. Titrations were carried out in alcohol-water solution using phenolphthalein as indicator.

TABLE V. Acrylonitrile - Vinyl 2-Ethylhexoate Copolymerizations. Mass Polymerization at 30° C.

Monomer, mole % acrylonitrile	Time at polymerization temp., months	Conversion, wt. %	Nitrogen analysis	Copolymer, mole % acrylonitrile
88.4	2	3	24.64, 24.39	97.8
69.5	2	3	22.98, 23.10	95.5
47.5	2	3	20.03, 19.88	91.0
23.4	2	5.4	15.32	81.5
18.8	2	3.2	13.25	76.5

TABLE VI. Acrylonitrile - Vinyl Formate Copolymerizations. Mass Polymerization at 60°, 0.05% Bz_2O_2

Monomer, mole % acrylonitrile	Time at polymerization temp.	Conversion, wt. %	Nitrogen		Copolymer, mole % acrylonitrile
			I	II	
66.7	6 days	0.1	21.06	--	84.3
47.6	6 days	0.18	19.88	19.70	80.3
25.4	72 hrs.	0.1	14.72	14.29	63.3
13.12	24 hrs.	0.2	13.24	13.26	57.8

TABLE VII. Acrylonitrile - Vinyl Benzoate Copolymerizations. Mass Polymerization at 75°, 0.05% Bz_2O_2

Monomer, mole % acrylonitrile	Conversion, wt. %	Nitrogen		Copolymer, mole % acrylonitrile
		I	II	
86.8	0.2	22.88	22.94	95.0
71.3	5.0	21.67	21.42	92.5
53.6	1.6	19.07	18.73	87.5
23.3	2.2	12.08	12.18	70.8
13.2	2.0	8.75	8.70	58.0

TABLE VIII. Acrylonitrile - Acetoxystyrene Copolymerizations. Mass Polymerization at 75°, 0.05% Bz_2O_2

Monomer, mole % acrylonitrile	Conversion, wt. %	Nitrogen		Copolymer, mole % acrylonitrile
		I	II	
96.6	0.4	12.29	12.55	73.7
77.5	2.4	7.01	7.06	52.5
53.8	4.6	5.80	5.47	45.5
20.8	1.6	2.99	2.99	28.0
17.6	4.0	2.59	2.79	25.8

TABLE IX. Acrylonitrile - Allyl Chloride Copolymerizations. Mass Polymerization at 60°, 0.1% Bz_2O_2

Monomer, Mole % acrylonitrile	Time at polymerization temp., hrs.	Conversion, wt. %	Nitrogen		Copolymer, mole % acrylonitrile
			I	II	
68.4	8.0	2.2	22.15	22.28	88.2
59.0	8.0	2.0	21.30	21.64	86.0
38.2	144.0	0.6	17.10	17.49	73.3
13.84	144.0	0.2	10.57	10.65	49.0
7.08	68.0	0.4	8.15	8.30	39.4

TABLE X. Vinylidene Chloride - Vinyl Benzoate Copolymerizations. Mass Polymerization Using No Catalyst

Monomer, mole % vinylidene chloride	Time at polymerization temp., hrs.	Conversion, wt. %	Polymerization Temp., °C.	Chlorine analysis	Copolymer, mole % vinyliodene chloride
93.2	3.75	< 3	24	69.90	96.95
82.1	5.0	< 3	24	68.82	95.94
69.6	72.5	< 3	24	66.31	93.60
21.2	216.0	< 3	50	40.43	65.28
7.4	483.0	< 3	50	23.90	42.60

TABLE XI. Vinylidene Chloride - Methyl Isopropenyl Ketone Copolymerizations. Mass Polymerization Using No Catalyst at 60° C.

Monomer, mole % vinylidene chloride	Conversion, wt. %	Chlorine analysis	Copolymer, mole % vinylidene chloride
95	< 3	59.20	75.5
75	< 3	34.67	39.4
50	< 3	16.46	17.2
25	< 3	7.68	7.8
5	< 3	2.92	2.9

TABLE XII. Vinyl Chloride - Vinyl Isobutyl Ether Copolymerizations. Mass Polymerization at 50° C. Using 1.0% Bz_2O_2

Monomer, mole % vinyl chloride	Time at polymerization temp., hrs.	Conversion, wt. %	Chlorine analyses		Copolymer, mole % vinyl chloride
			I	II	
96.82	1.25	1.0	55.70	56.06	99.0
93.51	1.25	1.0	55.96	55.62	98.9
87.44	16.0	2.7	49.20	49.69	91.5
71.47	16.0	3.0	43.58	43.91	84.3
51.19	16.0	3.7	37.37	37.25	75.1
7.78	16.0	1.0	21.16	21.47	49.0

TABLE XIII. Styrene - Citraconic Anhydride Copolymerizations. Mass Polymerization at 60°C. Using No Catalyst

Monomer, mole % styrene	Conversion, wt. %	Analyses				Copolymer, mole % styrene
		Carbon		Hydrogen		
		I	II	I	II	
95	< 3	81.38	81.18	6.62	6.58	73.3
75	< 3	77.41	77.29	6.44	6.22	63.8
50	< 3	73.17	72.81	6.25	6.08	53.2
25	< 3	70.98	70.67	6.43	5.98	48.3
5	< 3	69.81	69.49	5.67	5.43	44.1

substitution in the differential copolymer equation (6,7). This method gives more weight to the individual contributions of all experimental points than the intersecting method of Mayo and Lewis. The reactivity ratios for these systems and azeotropic compositions where they exist are given in Table XIV.

It is of interest that the azeotrope of the system styrene-methacrylic acid (74%) occurs at a much higher acid concentration than that of styrene-acrylic acid (48%). This difference is reflected in Q and e values of methacrylic acid as calculated from the Price and Alfrey relationship (1):

$$r_1 = \frac{Q_1}{Q_1} e^{-e_1(e_1-e_2)}$$

$$r_2 = \frac{Q_2}{Q_1} e^{e_2(e_1-e_2)} = \frac{Q_2}{Q_1} e^{-e_2(e_2-e_1)}$$

	Q_1	e_1
Acrylic acid*:	1.58 ± 0.05	1.0 ± 0.05
Methacrylic acid*:	2.0 ± 0.1	0.7 ± 0.05

These values may be interpreted as evidence of higher resonance stability of the radical adduct formed from methacrylic acid than from acrylic acid, and lower polarity of methacrylic acid than acrylic acid.

It will be noted that an azeotrope occurs in the system vinyl acetate-crotonic acid, but not in vinylidene chloride-crotonic acid. The cause for this is probably due to the higher resonance stability of radical adducts from vinylidene chloride than from vinyl acetate.

The data on acrylonitrile copolymerization with vinyl formate and vinyl 2-ethylhexoate supplements the vinyl acetate-acrylonitrile copolymerization data ($r_1 = 0.02 \pm 0.02$, $r_2 = 6 \pm 2$) reported previously (2). It will be noted that vinyl ester reactivity in copolymerization diminishes as the chain length increases. The comparatively high r_1 value (0.05 ± 0.005) of the vinyl benzoate-acrylonitrile system indicates a contribution of the aromatic nucleus to radical adduct stability even though no conjugation of the vinyl group exists.

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*Based on styrene values of Q = 1; e = -0.8.

The system α - acetoxystyrene-acrylonitrile shows that the polar and steric effects of an α -acetoxy group in styrene are of little importance in copolymerization with acrylonitrile (2). Conjugation of the vinyl group with the phenyl nucleus is the major factor in copolymerization of styrene derivatives.

Allyl chloride exhibits an expectedly low tendency to copolymerize with acrylonitrile. The copolymerization of vinylidene chloride and vinyl benzoate shows a lower resonance stabilization of vinyl benzoate than vinylidene chloride.

The copolymerization of methyl isopropenyl ketone and vinylidene chloride shows the considerable effect of vinyl ketone conjugation on resonance stabilization.

TABLE XIV.

	r_1	r_2	Composition (8.) of azeotrope in % M_2
Styrene-methacrylic acid	0.15 ± .01	0.7 ± 0.05	74
Styrene-acrylic acid	0.15 ± .01	0.25 ± 0.02	48
Crotonic acid-vinylidene chloride	0.065 ± .005	35 ± 5	--
Vinyl acetate-crotonic acid	0.3 ± .05	0.01 ± 0.01	44
Vinyl 2-ethylhexoate-acrylonitrile	0.01 ± .01	12 ± 2	--
Vinyl formate-acrylonitrile	0.04 ± .005	3.0 ± 0.05	--
Vinyl benzoate-acrylonitrile	0.05 ± .005	5.0 ± 0.05	--
- Acetoxystyrene-acrylonitrile	0.4 ± .05	.08 ± 0.01	40
Allyl chloride-acrylonitrile	0.05 ± .01	3.0 ± 0.2	--
Vinyl benzoate-vinylidene chloride	0.1 ± .02	7.0 ± 1	--
Methyl isopropenyl ketone-vinylidene chloride	4.5 ± .1	0.15 ± 0.02	--
Vinyl chloride-vinyl isobutyl ether	2.0 ± .2	0.02 ± 0.01	--
Styrene-citraconic anhydride	0.15 ± .02	0.01 ± 0.01	44

The copolymerization of vinyl chloride and vinyl isobutyl ether indicates that vinyl isobutyl ether has an even lower resonance stabilization of its adduct than vinyl chloride. The ready formation of this copolymer is interesting in view of the fact that, according to our own observations vinyl isobutyl ether will not polymerize alone by free radical catalysis.

The copolymerization of styrene and citraconic anhydride was found to yield a copolymerization curve similar to that of styrene-maleic anhydride previously reported by Alfrey (8). It appears that citraconic anhydride is slightly less reactive toward a styrene free radical than maleic anhydride.

EXPERIMENTAL

Styrene monomer. Redistilled Monsanto Chemical Co. material was used

Acrylonitrile was the redistilled product of American Cyanamid Co.

Methacrylic acid was the redistilled Rohm and Haas product.

Acrylic acid was the redistilled Rohm and Haas product.

Vinylidene chloride was the redistilled Dow Chemical Co. product.

Vinyl isobutyl ether was the redistilled General Aniline Corp. product.

Crotonic acid was obtained from Shawinigan Chemical Corp. and used as received.

Allyl chloride was the redistilled Shell Chemical Corp. product.

Benzoyl peroxide. The Lucidol Corp. product was used as received.

Copolymerization Method

Essentially the same experimental procedure was used for determining all monomer-copolymer relationships. A total of 100 g. of mixed monomers was placed in 4 oz. French square bottles with the desired quantity of benzoyl peroxide. The concentrations used are shown in Tables I-XIII. The air above the reaction mixture was swept out with nitrogen and the bottle was closed with a metal cap. Polymerization times and temperatures are described in Tables I-XIII. An air oven regulated to ±1° was used, and polymerization was interrupted at the point of slight viscosity increase or appearance of insoluble polymer (as in the case of copolymers containing above 60% acrylonitrile). The copolymer formed was isolated by pouring the reaction mixture into 3000 ml. of denatured ethanol (2B) at room temperature or into hexane in case of acrylic acid, methacrylic acid, or crotonic acid copolymers. Bottle rinsings were added to the precipitated mixture. The mixture was then boiled to render filtration easier and filtered. After triturating the copolymer with two successive quantities of 1500 ml. portions of ethanol, it was dried in an evaporating dish for two days in a circulating air oven at 60°C. and analyzed for nitrogen by the micro-Dumas method in the case of acrylonitrile copolymers, for carbon and hydrogen by combustion in the case of acrylic acid, methacrylic acid or citraconic anhydride copolymers, for chlorine by the Parr bomb method in the case of vinyl chloride or vinylidene chloride copolymers, or by acid number in the case of vinyl acetate-crotonic acid copolymers. Copolymerizations of vinyl chloride-vinyl isobutyl ether, vinylidene chloride-vinyl benzoate, and vinylidene chloride-crotonic acid were carried out in capped soda pop bottles under pressure. After the desired conversion was attained, pressure was released by puncturing the cap with an ice pick. Conversions and analyses for all copolymerizations are given in Table I-XIII.

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Synopsis

Information concerning monomer reactivity in copolymerization has been obtained for thirteen copolymerization systems. The influence of substituents and chain length in vinyl polymerization is discussed in the light of this and preceding data. Unsaturated acid behavior in copolymerizations is discussed for the first time.

Résumé

Des renseignements concernant la réactivité des monomères au cours des copolymérisations ont été obtenus pour treize systèmes de copolymérisation. L'influence des substituants et de la longeur de chaîne au cours des polymérisations vinyliques est discutée à la lumière de ces résultats précédents. Le comportement d'acides non-saturés dans les copolymérisations est discutée pour la première fois.

Zusammenfassung

Die Reaktivitaet von Monomeren in Mischpolymerisationen wurden fuer dreizehn Mischpolymerisationssysteme untersucht. Der Einfluss von Ersatzgruppen und Kettenlaenge auf Vinylpolymerisationen wird auf Grund der neu erhaltenen und vorhergehenden Daten eroertert. Das Verhalten ungesaettigter Saeuren in Mischpolymerisationen wird zum ersten Mal besprochen.

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Influence of Molecular Weight on the Properties of Polystyrene. I. Mechanical Properties of Polystyrene Films Cast from Solvents[1]

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INTRODUCTION

In the course of a major program on determining the relationships between physical and mechanical properties and the molecular weight of polystyrene, the problem of drying films cast from solvents was met. Previous investigators have shown (1,2,4) how difficult it is to remove the last traces of solvent so that the physical properties of the dry polymer itself can be measured.

The purpose of this undertaking was three-fold: to find a reproducible way to cast polystyrene films of the desired dimensions, to find a drying cycle which would reduce the solvent concentration to some small value which did not affect the measured mechanical properties within the precision of their determination, and to define that precision.

PREPARATION OF THE FILMS

Using a 2 x 2 block with replication design of experiment, with only four films, the relationships diagrammed in Figure 1 and listed below could be evaluated:

A. Reproducibility of casting procedure from methyl ethyl ketone (MEK).
B. Reproducibility of casting procedure from benzene.
C. Reproducibility of leaching procedure of MEK films.
D. Reproducibility of leaching procedure on benzene films.
E. Comparison of MEK films with benzene films.
F. Comparison of leached MEK films with leached benzene films.
G. Determination of effect of leaching on MEK films.
H. Determination of effect of leaching on benzene films.

Hence, two films 8 1/2 x 11 x 0.011 inches were cast on each of two days, one from benzene and one from MEK solution. The polystyrene had an intrinsic viscosity of 1.59 deciliters/g. measured at

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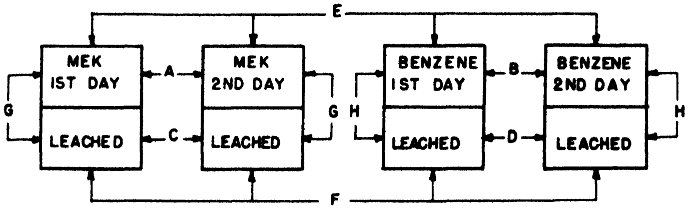
[1] Contribution from Plastics Research Laboratory, Monsanto Chemical Company, Springfield, Massachusetts. Presented at the American Physical Society, 1949, New York Meeting.

28.5°C. in toluene and a number-average molecular weight of 550,000. The solutions were made up to 7.5 grams polymer per 100 ml. of solution, filtered, and poured onto clean mercury retained by a stainless steel rectangular frame. The solutions were then covered and the solvent allowed to evaporate slowly for 2-3 days. Faster drying caused the surface of the film to assume an orange peel aspect.

FIGURE I

RELATIONSHIPS INVESTIGATED



The films after being removed from the mercury and frame were air dried overnight and dried for four hours in a vacuum oven at 50°C. Each film was split in half; one half of each was leached in methanol for two hours then air dried for two hours. All eight pieces were placed between separate cardboards and dried for one hour at 70°C. and four hours at 95°C.

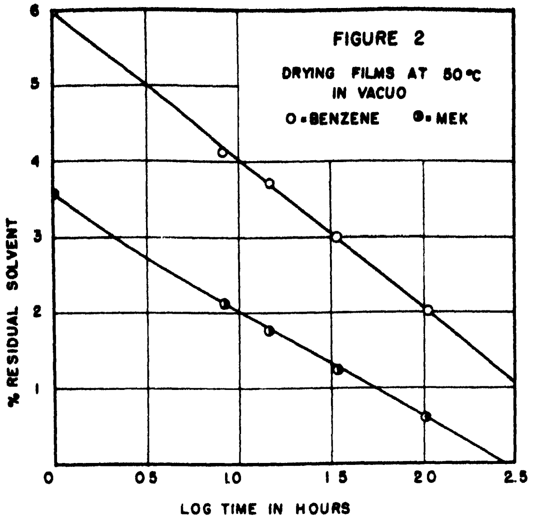
While the physical properties of these films were being tested, other drying experiments were made on extruded polystyrene film which had never been exposed to solvents. Eight pieces of film 0.0025 inches thick were cemented into two films each 0.010 inches thick. For one set, MEK was used as cement, for the other benzene. Each film was then dried in air overnight. The graph of percent residual solvent versus log time for drying at 50°C. in a vacuum oven is given in Figure 2. Another set of these films was made up, dried in air overnight and then dried at 87°C. in a circulating air oven. (Above 90°C. the films would shrivel up due to release of orientation strains (3)). The graph of percent residual solvent versus log time for this drying cycle is given in Figure 3.

Further drying treatments given to the cast films were based on the results of the above work and are given in detail below in the sections on physical measurements.

MEASUREMENT OF MECHANICAL PROPERTIES

1. Tensile Strength and Elongation

The tensile strengths and elongations were measured on strips 5 x 0.500 x 0.011 inches nominal size on a Scott IP-4 Tester at a nominal testing speed of 6000 p.s.i./min. Six replications were performed. These strips broke in the grips frequently so the grips were padded with polyvinyl chloride sheet stock. Dumbbell-shaped speci-



mens would have been more satisfactory but there was not sufficient material from which they could be cut.

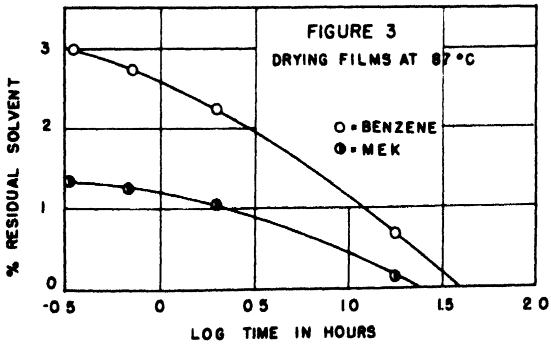
The results are given in Table I. In all cases the elongations were approximately 2% with a 100% error in measurement.

From these results the correlations as diagrammed in Figure 1 would be evaluated as (letters in parentheses refer to the key of Figure 1):

The tensile strengths of the films cast on the first day are higher than those cast on the second day (A,B). Leaching with methanol has no apparent effect (C, D, F, G, H) and hence is reproducible. Films cast from benzene have uniformly lower tensile strengths than films cast from MEK (E).

2. Dynamic Modulus and Damping

Dynamic mechanical properties are those in which the applied forces vary with time, in general in a sinusoidal manner. Two important dynamic constants are the dynamic Young's modulus and damping. The modulus in an inverse measure of the tensile elongation per unit of sinusoidally varying applied force, that is, it is a measure of the potential energy stored in the material when it is deformed. The damping indicates how much of the energy put into deforming the



system is not recoverable when the applied force is removed and is, therefore, transformed into heat energy, thus tending to heat up the material.

TABLE I. Tensile Strength of Films

Type of film			Mechanical property	
Solvent from which cast	Day cast	Treatment[1]	Tensile strength[2]	Standard deviation
Benzene	First		5790	115
Benzene	First	Leached	5650	110
MEK	First		5980	40
MEK	First	Leached	5500[3]	220
Benzene	Second		5220	290
Benzene	Second	Leached	5220	290
MEK	Second		5760	75
MEK	Second	Leached	5630	250
Benzene	Second	Dried 88 hrs. at 93° C.	6000	160
MEK	Second	Leached, dried 88 hrs. at 93° C.	6000	230

[1] Other than standard treatment described in the section on film preparation.

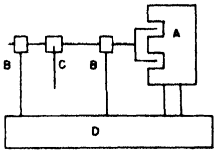
[2] Average of six determinations.

[3] These samples broke in the grips as well as between the fiducial marks so this value is probably low.

Figure 4 is a sketch of the dynamic testing apparatus used. A 12 inch permanent magnet loudspeaker was modified and used as a vibrator for the plastic film, which was in the form of a reed 3/8 in. wide and about 2 1/4 long. One end of the reed was clamped to the vibrator forming a cantilever beam. The power to drive the vibrator came from a 10 watt, high fidelity audio amplifier, which in turn was driven by a Hewlett-Packard model 200D audio oscillator. The

FIGURE 4

DYNAMIC TESTING APPARATUS



A: SPEAKER COIL AND MAGNET
B: LEAF SPRINGS
C: SAMPLE REED
D: HEAVY BASE

dynamic modulus was determined from the resonance frequency of the reed while the damping was obtained from the half-width of the resonance peak. For these measurements a low power microscope with a micrometer eyepiece was used to observe the deflection of the free end of the reed. The temperature was controlled by a windowed electric oven built around the reed. Vigorous air currents could not be tolerated in the oven since they would disturb the reed. Because of temperature gradients in the oven, the higher temperatures are indefinite by about two degrees.

By changing the dimensions of the reed the frequency range from 10 to 200 cycles per second could be studied except near 45 cycles per second where the vibrator itself had a natural frequency of vibration.

For a cantilever beam of rectangular cross-section with small damping, the dynamic Young's modulus can be calculated from the equation (6):

$$E = 38.24 \quad \frac{l^4}{d^2} \rho f_r^2$$

where E = Young's modulus, dynes/cm.^{2}; l = free length of reed, cm.; d = thickness of the reed, cm.; ρ = density of the reed, g./cc.; f_r = resonance frequency, cycles/second.

The damping can be found from the half width of the resonance peak. This quantity $\Delta f/f_r$ is the difference between the two frequencies at which the amplitude of vibration is one half the amplitude at the resonance frequency (where the amplitude is a maximum) divided by the resonance frequency. Damping can be expressed by many different terms depending on the experimental method of measuring it. In order to compare results obtained by different methods, it seems advisable to convert all the results to a common basis; the imaginary elastic modulus divided by the real elastic modulus is likely the best quantity for this. Young's modulus can be defined by:

$$E = E' + iE''$$

where E' is the real part of the modulus, E'' is the imaginary part of the modulus, i.e., a damping term, and i $(-1)^{1/2}$. It can be shown that the following equation is true if the damping does not become too great:

$$\frac{\Delta f}{f_r} = (3)^{1/2} \frac{E''}{E'}$$

If the terminology of the electrical analogs is adopted, E'' is the mechanical loss factor and E''/E' is the mechanical dissipation factor.

Table II gives the dynamic modulus and mechanical dissipation factor for some of the polystyrene films studied. Figures 5, 6, and 7 are graphs of the same data as a function of temperature. For a given specimen the relative accuracy of the modulus is about 2 percent while the error may be as large as 5 percent when comparing different specimens. The error in damping should be less than 10 percent. All the test were run at a frequency between 20 and 30 cycles per second, other tests have shown the modulus and damping for polystyrene to be nearly independent of frequency.

TABLE II. Dynamic Properties vs. Temperature

Type of film			Mechanical property			
Solvent from which cast	Day cast	Treatment[1]	Temp., °C.	Young's modulus, (dynes/cm.^{2}) x 10^{-10}	Dissipation factor	Symbol in Figs. 5,6, 7
Benzene	First		27	3.21	0.027	○
			55	2.89		
			63	2.83		
			73	2.59		
			80	2.27	0.079	
Benzene	First	Leached	30	3.23	0.027	◐
			52	2.92		
			60	2.83	0.042	
			71	2.62		
			76	2.49	0.064	
			81	2.28	0.093	
MEK	First		26	3.15	0.023	●
			50	2.89		
			61	2.80	0.035	
			70	2.68		
			78	2.60	0.043	
			86	2.44	0.051	
MEK	First	Leached	26	3.13	0.024	△
			55	2.81		
			62	2.72		
			77	2.50		
			80	2.44	0.046	
			85	2.35	0.054	
Benzene	Second		25	3.19	0.029	◭
			50	2.96		
			60	2.80		
			70	2.66	0.043	
			76	2.47	0.055	
			78	2.37	0.084	
MEK	Second	Leached	26	3.08	0.028	▲
			50	2.88		
			60	2.75		
			71	2.63	0.038	
			79	2.43	0.044	
			87	2.26	0.066	
Benzene	-	24 hrs. at 105° C.	28	3.24	0.026	□
			51	3.04		
			61	2.97		
			71	2.90	0.034	
			77.5	2.84	0.040	
			88	2.61	0.053	
			93	2.39	0.082	
			99	1.96	0.17	
Benzene	-	Dried 88 hrs. at 93° C.	28	3.40	0.027	◧
			50.5	3.18		
			60	3.10		
			70	2.99	0.036	
			78	2.88	0.039	

TABLE II (continued)

Type of film			Mechanical property			
Solvent from which cast	Day cast	Treatment[1]	Temp., °C.	Young's modulus, (dynes/cm.^{2}) x 10^{-10}	Dissipation factor	Symbol in Figs. 5,6, 7
			85	2.69	0.050	
			91	2.38	0.059	
MEK	-	Leached, dried 88 hrs. at 93° C.	27	3.16	0.024	■
			51	2.97		
			61	2.91		
			71	2.80	0.029	
			78	2.74	0.032	
			86.5	2.65	0.033	
			93	2.54	0.043	

---

[1] Other than standard treatment.

From these dynamic tests the relationships diagrammed in Figure 1 can be evaluated as follows (letters in parentheses refer to the key of Figure 1).

The casting procedure is fairly reproducible from day to day, whether using benzene or MEK as solvent (A, B). Leaching with methanol seems to have little effect and as such should be reproducible (C, D, F, G, H). All the films are nearly identical at room temperature but the moduli begin to decrease rapidly and the dissipation factors begin to increase rapidly for the benzene films at somewhat lower temperatures than for the MEK films (E).

3. Creep Measurements

The tensile creep of 5 x 0.5 x 0.011 inch strips of polystyrene films was measured at 79 ± 1°C. in an air bath. Elongation as a function

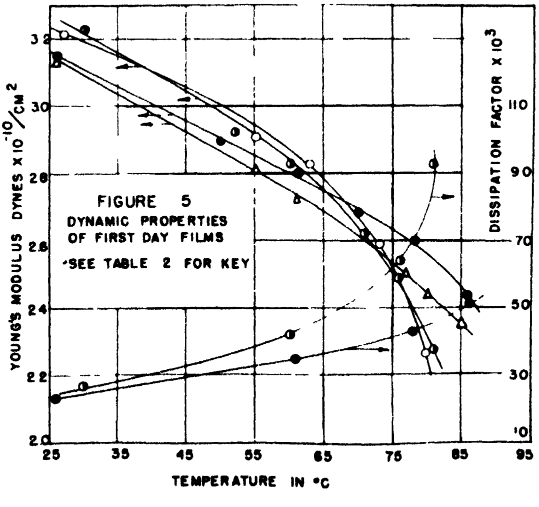
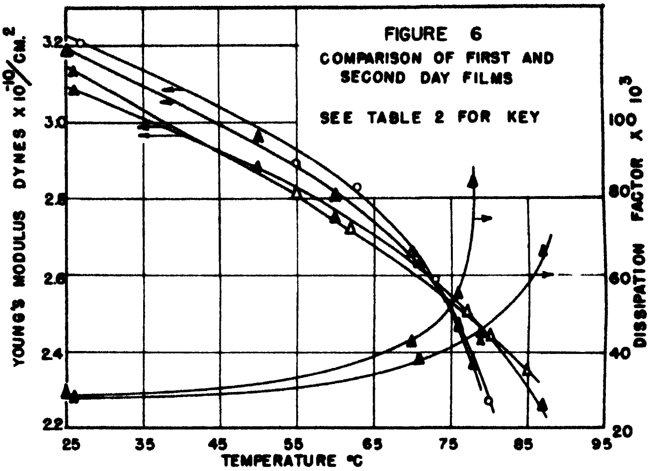
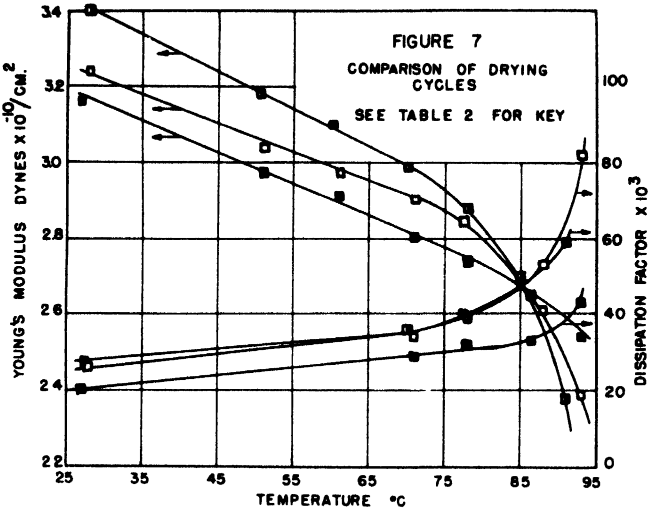


FIGURE 5
DYNAMIC PROPERTIES OF FIRST DAY FILMS
*SEE TABLE 2 FOR KEY





of time was followed with a cathetometer reading to 0.005 cm. focused on two fiducial ink marks about 4 cm. apart. The description of samples run and identifying symbols are given in Table III. Creep curves for all of the first day films are given in Figure 8. A comparison of the films cast on different days is given in Figure 9. Figure 10 illustrates the effect of various drying times and temperatures. The precision of the creep measurements was not evaluated in detail but the results are considered reliable within ±15% with the exception of the MEK film which had been dried for six days at high temperatures. This film did not creep appreciably before breaking.

The relationships diagrammed in Figure 1 can be evaluated from the creep results as follows (letters in parentheses refer to the key of Figure 1).

The films cast from MEK on different days are slightly different in their position along the compliance axis although this difference is practically within experimental error (A). The benzene films cast on different days besides being displaced along the compliance axis also have a differently shaped creep curve (B). Leaching with methanol seems to remove enough solvent to lower the rate of creep of both benzene and MEK films (G, H) but since this effect is of the same order of magnitude as the variations due to casting on different days the various reproducibilities of the leaching procedure were not evaluated (C, D, F). The MEK films in all cases had a smaller rate of creep than the benzene films and in addition seemed to give a creep curve with more concavity toward the time axis (E).

TABLE III. Summary of Creep Measurements

Type of film			Data to be found in:	
Solvent from which cast	Day cast	Treatment[1]	Figure number	Symbol
Benzene	First		8, 10	○,○
Benzene	First	Leached	8, 9	◑,◑
MEK	First		8, 9	△,△
MEK	First	Leached	8	△
Benzene	Second	Leached	9	○
MEK	Second		9, 10	◮,◮
Benzene		Dried 88 hrs. at 93° C.	10	◑
Benzene		Dried 88 hrs. at 93° C. and 24 hrs. at 103° C.	10	△
MEK		Leached, dried 88 hrs. at 93° C.	10	●
MEK		Leached, dried 176 hrs. at 93° C.	10	▲

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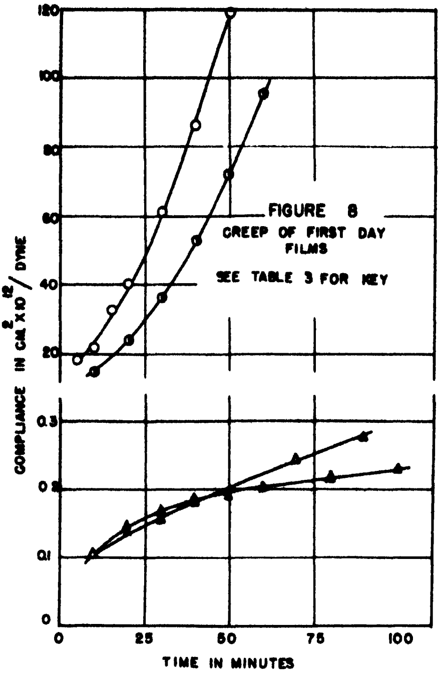
[1] Other than standard treatment.

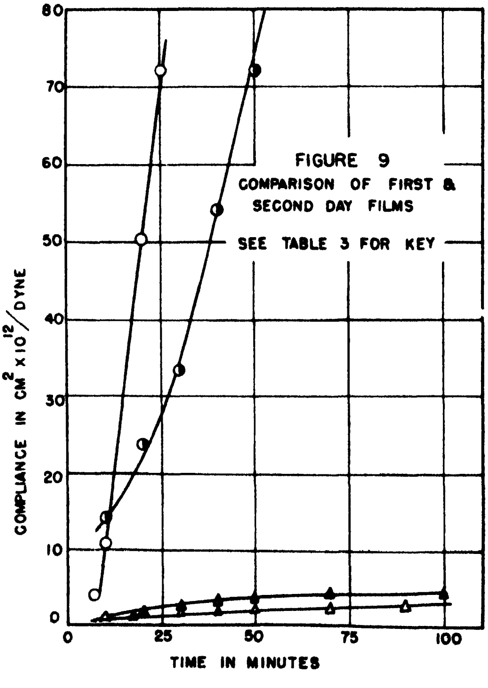
EFFECT OF PROLONGED DRYING

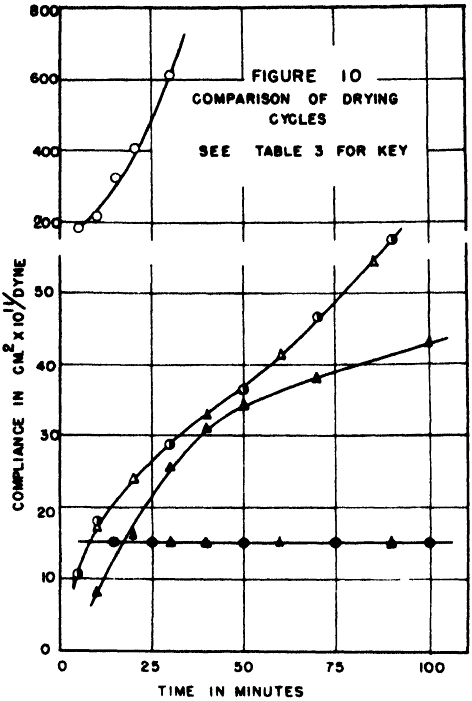
Guided by the results obtained from the drying experiments on extruded film, the films were then subjected to various drying times at temperatures above 90°C. Tensile strength measurements on films which had been dried for 88 hours at 93°C. showed that unleached and leached MEK films both were dried sufficiently to give the same tensile strength (Table I). Dynamic measurements of the same films showed that the benzene films had a higher modulus than the MEK films but that the modulus began to break off at a lower temperature (T_M) (Figure 7). The T_M was raised by the drying treatment for both benzene and MEK films.

The creep results, which showed up small differences in the films more strikingly, again showed that this drying treatment reduced the rate of creep considerably and also altered the shape of the creep curve for both benzene and MEK films (Figure 10). A benzene film which had been dried an additional 24 hours at 103°C. and an MEK



film which had received an extra 88 hours at 93°C. were identical with the films which had been dried for only 88 hours at 93°C. For these measurements of mechanical properties then, drying the films for approximately 3 days at temperatures above 90°C. reduces the solvent concentration to a value too small to affect the measurements within experimental error.





DISCUSSION

Although these polystyrene films have been shown to be dry in the sense that further drying does not alter the values of the mechanical properties measured, the films cast from benzene are different from those cast from MEK. In Figure 10, the creep curves of the benzene films have a much larger compliance than the MEK films and also the compliance increases with time which is not the case with dry MEK films. The question of to what this is due naturally arises. Considering the choice of possible effects to be those of film structure or residual solvent, the conclusion must be drawn that this effect is due to small amounts of tenaciously held benzene, since it is known (1) that 88 hours at 93°C. is sufficient to remove from these films even so gross a structure difference as orientation. The experiments detailed above unfortunately give little insight into the nature of this tight binding of benzene in thin polystyrene films.

A brief consideration of the results given in Figures 5, 6, and 7 seems to be in order as these data might throw some light on the as yet rather poorly understood mechanism of deformation of rigid polymers below and near the so-called second-order transition point.

The absolute value and the temperature dependance of the modulus of elasticity between 20 and 80°C. show clearly that polystyrene behaves very much like a great many organic or inorganic amorphous solids of high or low molecular weight; i.e., the deformations under static and dynamic stresses are determined primarily by the displacement of atoms (or molecules) rather than chain segment rearrangement. The small amount of long time creep under static stress which has been observed within this temperature (8) must then be attributed to a kind of slippage similar to the mechanism of creep in the metals (9). This interpretation of creep below 80°C. is further supported by several other experimental facts: low temperature creep polystyrene is almost always associated with crazing (8), low temperature creep is very much dependent on the method of fabrication and preparation of the test specimen in contrast to high temperature (8,10), and low temperature creep seldom, if ever, exceeds 2% elongation.

However, once a certain temperature, T_M, has been reached, the modulus decreases by several orders of magnitude and the mechanical loss factor first increases by several hundred percent and then decreases again (10) within a fairly narrow temperature range (30-40°C.). Although the change in modulus and loss factor is not discontinuous with temperature, it is sharp enough to suggest a definite change in the deformation mechanism requiring the simultaneous cooperation of practically all of the molecules. The rather marked influence of very small amounts of solvents on the onset of this transition and also on the creep (1) would then have to be interpreted as an impurity effect decreasing the stability of the system toward dynamic or static stress.

The temperature range in which the mechanical properties undergo a rather sudden transition is just about when the so-called second-order transition point for polystyrene has been established on the basis of volumetric (5) and refractometric (11) measurements as a function of rate of temperature increase or decrease. The fact that the absolute value of the transition point depends on the rate of heating (or cooling) and furthermore that the transition point completely disappears when the rate of heating approaches zero has lent considerable support to the belief that this point is not a transition point in the thermodynamic sense but only an apparent discontinuity due to a rate process which is determined by the very high viscosity of the medium. However, it does not seem reasonable to assume that this close relationship between the two phenomena is purely accidental. It appears more justified to consider both processes as being governed by the same mechanism with the proviso that the interpretation of volumetric second-order transition point is complicated by the superposition of a non-equilibrium process on an equilibrium process (7).

CONCLUSIONS

Using a stringent drying cycle, it has been shown that the procedure used for casting polystyrene films is reproducible from day to day whether using MEK or benzene as solvent. Methanol leaching to remove solvent is not very efficient.

The precision of the tensile strength, creep, and dynamic modulus and dissipation factor measurements has been evaluated.

The reason for the difference between "dry" benzene films and "dry" MEK films has been discussed.

A discussion of the second-order transition point and the point at which the dynamic modulus begins to decrease rapidly has been included.

Acknowledgment

We wish to acknowledge the continuing interest of Dr. N. N. T. Samaras in this work.

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Synopsis

The variables of casting polystyrene films from methyl ethyl ketone and from benzene are investigated. It is shown that stringent drying is necessary to remove the last traces of solvent. The differences in dry film structure, second-order transition point, and temperature at which the dynamic modulus suddenly decreases are discussed.

Résumé

Les différents facteurs, qui influencent le coulage de films de polystyrène au départ de solution dans la méthyléthylacétone et dans le benzène, ont été étudiés. Un séchage rigoureux est nécessaire pour éliminer les dernières traces de solvant. Les différences du point de vue de la structure du film sec, du point de transition de second ordre, et de la température, à laquelle le module dynamique décroît soudainement, sont discutées.

Zusammenfassung

Verschiedene Methoden, durch die Polystyrolfilme von Methylaethylketon und Benzolloesungen gegossen werden koennen, werden erforscht. Es wird gezeigt, dass ein wirksamer Trocknungsprozess notwendig ist, um die letzten Loesemittelspuren zu entfernen. Die Unterschiede in der Struktur der getrockneten Filme, ihrer Uebergangstemperatur der zweiten Ordnung und der Temperatur, bei der der dynamische Modul ploetzlich abnimmt, werden eroertert.

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Reactivity of Fibrous Cellulose

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In recent years, the results of several investigations have been published attempting to define the quality of fibrous celluloses by their reactivity (1-10). These publications may be considered as the outcome of the recognition that the suitability of cellulose fibers for chemical conversion purposes is closely related to the physical (supermolecular) structure of their building units.

The widely held view that cellulose molecules in fibers exist in a highly regular, less regular, and in randomly oriented arrangement led to the conception that regions in the fibers, where the cellulose chains are densely packed and regularly oriented, will react with solutions relatively slowly. Other portions of the fibers with an expanded structure, where the access of the reagents is greater, will react faster. Attempts have been made to determine the relative proportions of the difficultly and easily accessible areas in fibrous celluloses. These regions have also been considered to be essentially crystalline and amorphous, respectively. No sharp borderline seems to exist, however, between the extreme highly ordered and highly disordered areas, but there are apparently transitional regions present in which the organization of cellulose chains is of intermediate degrees (11-14).

KINETIC METHODS FOR ESTIMATING DIFFICULTLY AND EASILY ACCESSIBLE AREAS

One of the methods for estimating the relative proportions of crystalline and amorphous regions consists of submitting the cellulose fibers to a mild chemical reaction and following the progress of the reaction with time. The rate plots are then resolved with the underlying idea that they represent a slow reaction with the difficultly accessible component superimposed upon a fast reaction with the more reactive or easily accessible components. This kinetic method has been applied by several investigators and the rates of various mild reactions have been studied, with the assumption that the chemical reaction does not materially alter the physical structure of the fibers investigated. The disadvantage of the kinetic method, according to Purves, et al. (3,15), is that, due to penetration of the reagents to crystalline regions and swelling, the amorphous areas assessed may be too high. According to Mark et al. (10,16) by the application of aqueous solutions swelling may open some of the weak bonds between hydroxyl groups of adjacent chains, and as a result of an increased penetration increased degree of accessibility would be indicated. Yet the same authors do not exclude the possibility that during acid hydrolysis in the presence of ferric chloride some crystallization occurs which would tend to increase the amount of difficultly accessible areas in cellulose fibers when this method is used. Hermans (17) draws attention to the dependence of accessibility on the nature of reagent and solvent used, since the molecular size of the latter and affinity conditions towards cellulose may influence the amounts of crystalline and amorphous regions assessed by applying different reagents and solvents. In view of these facts it could be explained why the relative proportions estimated by kinetic methods disagree with those determined by physical methods (x-ray, infrared absorption, thallation, gas adsorption, etc.). On the other hand, it may be anticipated that the kinetic methods would have the advantage of throwing more light on the course and mechanism of heterogeneous reactions with fibrous cellulose, and a successful analysis of the results may even contribute to a better understanding of the fine structure of cellulose fibers.

HETEROGENEOUS ACID HYDROLYSIS OF CELLULOSE

The rate of the heterogeneous acid hydrolysis of fibrous cellulose — contrarily to the homogeneous — has received relatively little attention. Birtwell, Clibbens, and Geake (18) expressed the rate of hydrolysis of cotton fibers by the change in "copper-number" and advanced the rate equation:

$$\text{Copper number} = ct^n$$

where t is the time of hydrolysis, and c and n are constants. This rate equation, of rather an empirical nature, had only a limited validity and satisfied the experimental results for the early stages of hydrolysis. Yorston (19), on measuring the loss in weight with time for acid hydrolysis, arrived at the same rate expression, viz:

$$X = ct^m$$

where X is the percentage loss at the time t, and c and m are constants. The validity of this relation was also somewhat limited. Nickerson (1), and Conrad and Scroggie (5), using the method based on the evolution of carbon dioxide by the action of hydrochloric acid in the presence of ferric chloride, interpreted the hydrolysis-time plots as a superposition of a kinetically zero-order reaction upon a fast reaction. Lovell and Goldschmid (7), applying the method of measuring the loss in weight on subjecting cellulose samples to the action of hydrochloric acid plus ferric chloride, interpreted their results in a similar manner.

Philipp, Nelson, and Ziifle (20) and Nelson and Conrad (21) followed the loss in weight of cellulose fibers subjected to the action of 6N, 4N and 2.5N hydrochloric acid solutions at 95°C. and 100°C. By introducing a correction for humic substances formed under their experimental conditions, they formulated the hydrolysis of both crystalline and amorphous cellulose as concurrent first-order reactions. They derived values for the energy of activation of the hydrolysis of crystalline cellulose ranging from 34.6 to 35.0 kcal., and explain these relatively high values, when compared with lower values obtained by other authors, as being due to the different temperatures at which activation energies were determined. They did not compute the activation energy for the hydrolysis of amorphous cellulose because the first-order rate constants were not reliable enough for such computation. These authors maintain that neither acid concentration nor temperature has any effect on the amount of crystalline and amorphous cellulose as determined by their hydrolysis method.

EXPERIMENTAL

The method adopted for expressing the rate of removal of constituents from, and the reactivity of, cellulose fibers consisted of measuring directly the loss in weight on treating an amount of fiber, corresponding to 1 g. moisture free, with 150 ml. of 8% hydrochloric acid solution at different temperatures for different periods of time. The sample was placed in an Erlenmeyer flask provided with a reflux air condenser and kept in a constant temperature oil bath. The acid solution was preheated to a temperature of 1-2 degrees high-

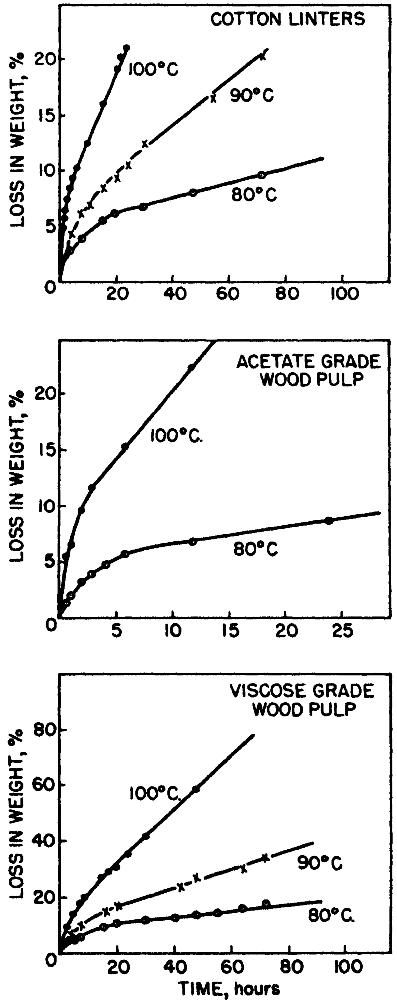

Fig. 1. Hydrolysis-time curves of cellulose fibers.

er than the reaction temperature before being added to the fibers. No ferric chloride was used and the reaction mixture was not stirred. After a predetermined period of time the reaction mixture was filtered rapidly through a sintered glass crucible, the insoluble residue washed with hot water, and dried to a constant weight at 105°C.

The various cellulose samples used are described below, as follows:

1. Bleached cotton linters (commercial grade).
2. Acetate grade wood pulp (from Rayonier Corp., U.S.A.).
3. Viscose grade wood pulp (Scandinavian origin).
4. Hydrocellulose "A" (prepared from cotton linters by heating with 8% hydrochloric acid solution, filtering, washing, and drying in air).
5. Hydrocellulose "B" (prepared similarly to "A" but under milder conditions of hydrolysis).

INTERPRETATION OF DATA

The hydrolysis rates are illustrated in Figure 1, where the per cent loss in weight values are plotted against time (in hours) or hydrolysis of the fibrous celluloses. Figure 2 illustrates the rate of loss in weight of the hydrocellulose samples.

The rate plots have been resolved in accordance with the idea set forth above, i.e., extrapolating their straight parts to the ordinate and drawing a straight line through the origin with the same gradient.

That the resolving of the rate plots in this manner is justified is borne out by the results of hydrolyses of the hydrocellulose samples, since these rate plots are reasonably straight lines for almost

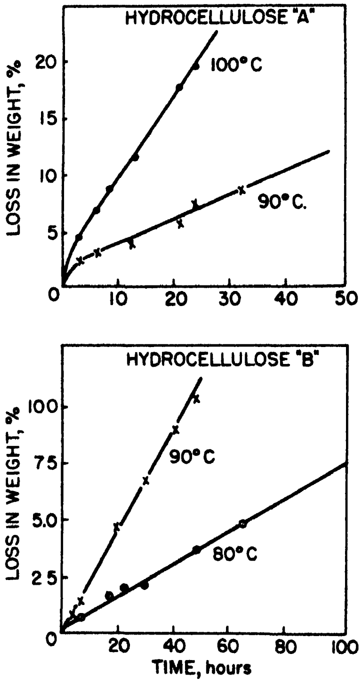

Fig. 2. Hydrolysis-time curves of hydrocelluloses.

the entire range (Fig. 2). Accordingly, the rate determining step in the reaction with the difficultly accessible components in the fibrous cellulose samples may be considered, within the experimental range investigated, as a kinetically zero-order reaction. The rate constant, which is the gradient of the straight part of the rate plots, corresponding to the experiments conducted at different temperatures is denoted by K_1. The rate of loss in weight (hydrolysis) of the difficultly accessible fraction of the fibers under the experimental conditions is:

$$\frac{dx_1}{dt} = K_1$$

Thus:

$$x_1 = K_1 t$$

where x_1 is the percentage difficultly accessible portion removed and t the time of hydrolysis.

The intercepts with the ordinate would represent the percentage of easily accessible components in the fibers, and the difference from a hundred the percentage difficultly accessible fraction. These values and the gradient of the straight part of the rate plots (rate constants K_1) are listed in Table I. In a separate column the ratio of these rate constants for 10°C. temperature difference is also shown, and in Figure 3. the $\log_e K_1$ values are plotted against $1/T$.

TABLE I. Accessibilities and Rate Constants for Removal of Difficultly Accessible Components of Cellulose Fibers and Influence of Temperature

Cellulose Fiber	Temperature of hydrolysis, °C.	Easily accessible components, %	Difficultly accessible components, %	K_1	Ratio of K_1 values for 10° C.
Cotton linters	100	6.8	93.2	0.59	2.95
	90	5.7	94.3	0.20	2.98
	80	4.7	95.3	0.067	
Acetate grade pulp	100	8.5	91.5	1.15	2.97
	80	5.0	95.0	0.14	
Viscose grade pulp	100	13.0	87.0	0.94	2.85
	90	10.1	89.9	0.33	3.00
	80	8.6	91.4	0.11	

Reaction with Difficultly Accessible Fraction and Its Reactivity

It will be observed that under the experimental conditions applied the rate of removal of the difficultly accessible portion of the cellulose fibers investigated has a relatively high temperature coefficient. The energy of activation computed by means of Arrhenius' formula amounts to 28-29 kcal./mol. Thus, the energy of activation of the rate-controlling reaction involved in the removal of the difficultly accessible portion is relatively high, and it may represent the energy of activation of the hydrolysis of cellulose.

The rate constants (K_1) of this reaction with the various representative celluloses at the same temperatures are different and hence the reactivity of the difficultly accessible components appears to be different in various fibers. Within the investigated range the temperature coefficient for 10°C. is, however, practically the same, irrespective of the nature of the fibrous samples. These were relatively pure cellulose fibers, although the wood pulps contained small quantities of pentosan materials.

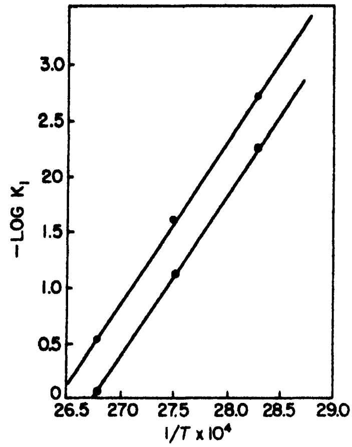

Fig. 3. Effect of temperature on rate constant of reaction with crystalline cellulose.

In comparing the rate constants (K_1) of the reaction with the difficultly accessible fraction of the samples, it appears that cotton linters contain the most unreactive or difficultly accessible components when compared with the wood pulps.

Reaction with Easily Accessible Fraction and Its Reactivity

The percentage of reactive components estimated varies greatly with the nature of the fibers, presumably depending on the fine structure of the parent fibers (plants), and on the processing conditions in making the pulps. As referred to above, in accordance with the contention of Purves and of Mark, the magnitudes of the easily and difficultly accessible areas assessed depend on the experimental conditions applied. For the same test sample the easily and difficultly accessible portions estimated are different for different temperatures. These findings seem to be in harmony with the conception that fibrous celluloses consist of a system of uneven surfaces with different accessibilities and without sharp boundaries (4, 11-14).

As mentioned in the introductory part of this paper Philipp, Nelson, and Ziifle (20) maintain that neither temperature nor acid concentration has any effect on the amount of crystalline and amorphous cellulose as determined by their method and that the differences are within the experimental error. While these authors varied the acid concentration between 2.5N to 6N, the temperatures applied were 95°C. and 100°C.

The easily accessible fraction of the cotton linters sample assessed by the method applied in the present work was the lowest when compared with the wood pulps. It may be mentioned that cotton linters usually are practically free of pentosans, while the wood pulps used contained such constituents. The greater part of the pentosans present in fibrous celluloses may be assumed to be amorphous or easily hydrolyzable (22).

In characterizing the reactivity of the easily accessible areas of fibrous celluloses, consideration should be given to the thought that their relative amounts may not be the most significant factor. If, in cellulose fibers, cross linkages are operative between adjacent chains or foreign groups are present within the cellulose molecules, then depending on the nature and distribution of these "irregularities" their reactivity may be significantly affected. The possibility of the presence of primary valence cross-linkages and of foreign groupings cannot be excluded from consideration (23,24). It may be of interest to mention that according to recent studies one weak link or "defect" is believed to be present in the cellulose chain molecules for every 500 glucose units (25,26,27), while another postulate is that one cross link of primary valence character is operative between the cellulose chains at distances corresponding to 548 glucose units (24). Thus it appears that the statement made in 1938 by Spurlin (28) is still valid: "The fiber structure is the most important as well as the least understood factor determining the nature of cellulose reactions."

The rate and molecular mechanism of the hydrolysis of the reactive or easily accessible components of cellulose fibers is rather complex in nature. Diffusion and adsorption phenomena seem to play an important role. In order to illustrate this, it may be mentioned that in evaluating the energy of activation for the removal of easily accessible components by the customary method, i.e., applying the time values corresponding to the same fraction of removal at different temperatures, irregular values for the energy of activation have been obtained. Taylor (29) recently suggested that adsorption on uneven surfaces may occur in such a manner that at a certain temperature one area is sensibly covered by adsorbed molecules while another area is practically bare, whereas at a different temperature other conditions may exist. The adsorbent (fibrous cellulose) thus may possess two (or more) distinct adsorbent areas characterized by two (or more) distinct activation energies. It may also be mentioned that by applying kinetic formulations for "retarded reactions" or "activated diffusion" (30) reasonably good approximations of the rate of removal of the easily accessible fractions may be offered, but further work is needed for the final mathematical formulation of the kinetics of this reaction.

Summary

1. On measuring the rate of loss in weight by hydrolyzing cellulose fibers and resolving the rate plots, the difficultly and easily accessible regions assessed are different with the same fibers, depending on the experimental conditions.

2. Under the experimental conditions applied, the rate of loss in weight by hydrolyzing hydrocelluloses is essentially a kinetically zero-order reaction, supporting the justification for resolving the rate plots for the hydrolysis of fibrous cellulose into a slow kinetically zero-order reaction and a fast reaction.

3. Within the experimental range investigated, the rate constant of the rate-controlling step in the hydrolysis of the difficultly accessible fraction of cellulose fibers with 8% hydrochloric acid solution has a relatively high temperature coefficient: 2.8-3 for a rise of 10°C. temperature.

4. The energy of activation of the rate-determining process with the difficultly accessible components of the representative cellulose fibers amounts to 28-29 kcal/mol.

5. Both the rate constant of the reaction with the difficultly accessible region and the relative proportions of difficultly and easily accessible fractions assessed by the kinetic method used may be useful for comparing the reactivity of different cellulose fibers.

6. By a successful formulation of the kinetics of hydrolysis of the reactive or easily removable components, the reactivity may be more adequately characterized.

Acknowledgment

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Addendum

The author wishes to emphasize that the subject of his paper has been in the center of recent research, the results of which were published after the date of submitting his manuscript to the editors of this journal. The relevant literature references could not be considered in the above paper.

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Synopsis

By applying hydrochloric acid solution at different temperatures to various fibrous cellulose samples and following the per cent loss in weight with time, hydrolysis-time curves have been obtained. These plots have been resolved into a straight line and a curve, representing the rate of removal of difficultly and easily removable components, respectively. Under the experimental conditions applied, the rate-determining reaction in the removal of the difficultly accessible components from the fibers is essentially a kinetically zero-order reaction. This was borne out by the results of hydrolyses of hydrocellulose preparations. Within the experimental range the temperature coefficient of this rate is independent of the representative fibrous materials and is relatively high, corresponding to an energy of activation of 28-29 kcal./mol. The easily and difficultly accessible regions, assessed by resolving the rate plots, are different with the same fibers, depending on the experimental conditions. The reactivity of both the easily and difficultly hydrolyzable constituents varies with different cellulose fibers. The complex nature of the kinetics of removal (hydrolysis) of the easily accessible components is discussed.

Résumé

Par traitement, à différentes températures, de différentes fibres cellulosiques par une solution d'acide chlorhydrique et en sui-

vant la perte en poids en fonction du temps, on obtient des courbes hydrolyse-temps. Ces courbes sont la résultante d'une ligne droite et d'une courbe, correspondant respectivement à la vitesse de déplacement des composants difficilement hydrolysables et à la vitesse de déplacement des composants facilement hydrolysés. Dans les conditions expérimentales indiquées, la réaction, qui détermine la vitesse de déplacement des composants difficilement accessibles, est essentiellement une réaction d'un ordre cinétique zéro. Ceci résulte d'expériences d'hydrolyse de préparations d'hydrocellulose. Le coëfficient thermique de la vitesse de réaction, dans les limites de températures envisagées, est indépendant du matériel fibreux examiné, et est relativement élevé; il correspond à une énergie d'activation de 28-29 kcal./mol. Les régions facilement et difficilement accessibles, déterminées au départ des courbes d'hydrolyse, sont elles-mêmes différentes pour une même fibre, suivant les conditions expérimentales. La réactivité, aussi bien des constituants facilement hydrolysables que des constituants difficilement hydrolysables, varie pour des fibres cellulosiques différentes. La nature complexe de la cinétique de l'hydrolyse des constituants, facilement accessibles, est soumise à discussion.

Zusammenfassung

Verschiedene Proben von Cellulosefasern wurden mit Salzsaeure bei verschiedenen Temperaturen versetzt und der Gewichtsverlust verfolgt; die Resultate wurden dann als Hydrolyse-Zeit Kurven dargestellt. Die Linien wurden in Gerade und Kurven zerlegt, die als ein Mass der leicht und schwer zu entfernenden Komponenten gedeutet wurden. Bei dem angewandten experimentalen Verfahren ist die Reaktion die die Geschwindigkeit der schwer von den Fasern zu entfernenden Bestandteile bestimmt, kinetisch eine Null-Ordnung Reaktion. Das wurde auch vom Ergebniss der Hydrolysen an Hydrocellulose-Preparaten unterstuetzt. Im Rahmen der experimentalen Temperaturen war der Temperatur-Koefficient dieser Geschwindigkeit unabhaengig von den representierenden Faserstoffen und war relativ hoch, einer Aktionsenergie von 28-29 Kcal./mol. entsprechend. Die leicht und die schwer zu erreichenden Bestandteile, die durch die Analyse der Geschwindigkeits-Kurven geschaetzt wurden, sind bei den selben Fasern verschieden, abhaengig vom experimentalen Verfahren. Die Reaktivitaet von sowohl den leicht also auch den schwer hydrolysierbaren Bestandteilen ist bei verschiedenen Fasern verschieden. Die Komplexitaet der Kinetik der Abspaltung leicht erreichbarer Bestandteile (Hydrolyse) wird eroertert.

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Copolymerization. II. Molecular Weight Distribution and Mean Molecular Weights in Copolymerization Systems

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THE FUNDAMENTAL EQUATIONS

In Part I a generalized reaction scheme has been proposed and the functions relating the rate of copolymerization to the several measurable quantities of the system worked out. The symbols employed below have already been defined (1) and are mostly self-explanatory by the use of the appropriate subscripts. It is convenient for mathematical manipulation to let:

$$k_{p_{r_{aa}}}(P_r) = x_r \quad \text{and} \quad k_{p_{r_{bb}}}(Q_r) = y_r \tag{1}$$

In the practically important case of mutual termination, the velocity coefficients are again assumed as the product of individual constants applying to each participating chain type, and the kinetic consequences considered according to the simplifying assumption (Eq. 2) and the more general assumption (Eq. 3).

$$k_{t_{rs_{ab}}} = k_{t_{r_a}} . k_{t_{s_b}} \tag{2}$$

$$k_{t_{rs_{ab}}} = k_{t_{r_{ab}}} . k_{t_{s_{ab}}} \tag{3}$$

The fundamental series of difference equations and the consequent rate equations given in Part I are rearranged into the following more suitable forms and classified according to the mode of termination.

Monomer Termination:

$$\frac{d[P_r]}{dt} = 0 = k_{p_{aa}}[P_{r-1}][A] + k_{p_{ba}}[Q_{r-1}][A] - k_{p_{aa}}[P_r][A]$$
$$- k_{p_{ab}}[P_r][B] - k_{t_{aa}}[P_r][A] - k_{t_{ab}}[P_r][B]$$

That is:

$$x_{r-1} + \frac{1}{\mu} . y_{r-1} = x_r \left\{ 1 + \frac{[B]}{\sigma[A]} + \lambda_a + \frac{[B]}{\sigma[A]} . \lambda_{ab} \right\} \tag{4a}$$

Similarly:

$$y_{r-1} + \frac{1}{\sigma}\cdot x_{r-1} = y_r \left\{1 + \frac{[A]}{\mu[B]} + \lambda_b + \frac{[A]}{\mu[B]}\cdot\lambda_{ba}\right\} \tag{4b}$$

Also:

$$\frac{d[A_{r+1}]}{dt} = [A]\left\{\lambda_a\cdot x_r + \frac{\lambda_{ba}}{\mu}\cdot y_r\right\} \tag{5}$$

Spontaneous Termination:

$$\frac{d[P_r]}{dt} = 0 = k_{p_{aa}}[P_{r-1}][A] + k_{p_{ba}}[Q_{r-1}][A] - k_{p_{aa}}[P_r][A] - k_{p_{ab}}[P_r][B] - k_{t_a}[P_r]$$

That is:

$$x_{r-1} + \frac{1}{\mu}\cdot y_{r-1} = x_r\left\{1 + \frac{[B]}{\sigma[A]} + \frac{\lambda_a}{[A]}\right\} \tag{6}$$

and:

$$\frac{d[A_r]}{dt} = \lambda_a\cdot x_r \tag{7}$$

Mutual Termination by Equation 2:

$$\frac{d[P_r]}{dt} = 0 = k_{p_{aa}}[P_{r-1}][A] + k_{p_{ba}}[Q_{r-1}][A] - k_{p_{aa}}[P_r][A] - k_{p_{ab}}[P_r][B] - k_{t_a}[P_r]\left\{\Sigma k_{t_a}[P_r] + \Sigma k_{t_b}[Q_r]\right\}$$

That is:

$$x_{r-1} + \frac{1}{\mu}\cdot y_{r-1} = x_r\left\{1 + \frac{[B]}{\sigma[A]} + \frac{\delta_a\,(X_a + X_b)^{1/2}}{[A]}\right\} \tag{8}$$

For disproportionation:

$$\frac{d[A_r]}{dt} = \delta_a\cdot x_r\left\{X_a + X_b\right\}^{1/2} \tag{9}$$

and for combination:

$$\frac{d[M_r]}{dt} = \left\{\frac{1}{2}\;\delta_a^2\sum_{s=1}^{r-1}x_s\cdot x_{r-s} + 2\delta_a\delta_b\sum_{s=1}^{r-1}x_s\cdot y_{r-s} + \delta_b^2\sum_{s=1}^{r-1}y_s\cdot y_{r-s}\right\} \tag{10}$$

Mutual Termination by Equation 3:

$$\frac{d[P_r]}{dt} = 0 = k_{p_{aa}}[P_{r-1}][A] + k_{p_{ba}}[Q_{r-1}][A] - k_{p_{aa}}[P_r][A] - k_{p_{ab}}[P_r][B] - k_{t_a}[P_r]\Sigma k_{t_a}[P_r] - k_{t_{ab}}[P_r]\Sigma k_{t_{ab}}[Q_r]$$

That is:

$$x_{r-1} + \frac{1}{\mu}\cdot y_{r-1} = x_r\left\{1 + \frac{[B]}{\sigma[A]} + \frac{\delta_a}{[A]}\cdot + \frac{\delta_a\sigma[A] + \varphi\,.\,\delta_b\mu[B]}{D^{1/2}}(X_a + X_b)^{1/2}\right\} \tag{11}$$

where:

$$D = \delta_a^2\sigma^2[A]^2 + 2\varphi\delta_a.\delta_b.\mu\sigma[A][B] + \delta_b^2.\mu^2[B]^2 \quad \text{by reference (1), Table II.} \qquad (12)$$

For disproportionation:

$$\frac{d[P_r]}{dt} = \delta_a.x_r.\frac{\delta_a\sigma[A] + \varphi\delta_b.\mu[B]}{D^{1/2}}\left\{X_a + X_b\right\}^{1/2} \qquad (13)$$

and for combination:

$$\frac{d[M_r]}{dt} = \frac{1}{2}\left\{\delta_a^2\sum_{s=1}^{r-1} x_s.x_{r-s} + 2\varphi\delta a\,\delta_b\sum_{s=1}^{r-1}x_s.y_{r-s} + \delta_b^2\sum_{s=1}^{r-1}y_s.y_{r-s}\right\} \qquad (14)$$

MOLECULAR WEIGHT DISTRIBUTION FUNCTIONS

In order to obtain the molecular weight distribution functions:

$$\int_{A_0+B_0}^{A+B} d[M_r] = \int_{A_0}^{A} d[A_r] + \int_{B_0}^{B} d[B_r]$$

the customary procedure is to derive the rate functions d $[A_r]$ /dt and d [A] /dt, and to integrate the differential equation:

$$d[A_r]/d[A] = \frac{d[A_r]/dt}{d[A]/dt}$$

It is apparent from equations 5,7,9,10,13, and 14, that the expression for d $[A_r]$ /dt is at once obtained when the values of x_r and y_r are found.

Solution of x_r and y_r

For all termination mechanisms, the equations 4, 6, 8, and 11 relating x_r, x_{r-1}, y_r, y_{r-1}, may be written:

$$k_1.x_{r-1} + k_2.y_{r-1} = k_3.x_r$$

$$k_4.x_{r-1} + k_5.y_{r-1} = k_6.y_r$$

where $k_1 = 1$, k_2, $= 1/\mu$, $k_4 = 1/\sigma$, $k_5 = 1$ in all cases, and $k_3 = 1 + m_1 + n_1$, and $k_6 = 1 + m_2 + n_2$. For all cases, $m_1 = [B]/\sigma[A]$; $m_2 = [A]/\mu\ B$.

The values of n_1 and n_2 depend on the mode of termination, being respectively for monomer, spontaneous, and mutual termination in the case of n_1:

Monomer Termination: $\lambda_a + \dfrac{n_1}{m_1\lambda_{ab}}$

Spontaneous Termination: $\lambda_a/[A]$

Mutual Termination by equation 2: $\delta_a\left\{X_a + X_b\right\}^{1/2}/[A]$

Mutual Termination by equation 3: $\dfrac{\delta_a\left\{\delta_a\sigma[A] + \varphi.\delta_b\mu[B]\right\}}{[A]\quad D^{1/2}}\left\{X_a + X_b\right\}^{1/2}$

Since the rate of termination is much less than the rate of propagation, n_1 and n_2 are $\ll 1$, while m_1 and m_2 are comparable with unity. In simplifying the algebra below, the fact that:

$$n_1 \text{ and } n_2 << m_1 \text{ and } m_2$$

is essential. We also have that:

$$m_1.m_2 = k_2.k_4$$

The series of equations represented by 15 are of the class known as difference equations, for the solution of which exist standard mathematical techniques.

Obtaining x_r, and x_{r-1} in terms of y_{r-1}, y_r, and y_{r+1} from equation 15b and substituting in equation 15a, an equation wholly in the variable y_r is given:

$$a.y_{r+1} - b.y_r + c.y_{r-1} = 0 \tag{16}$$

where:

$$a = k_3.k_6,\ b = k_3.k_5 + k_1.k_6,\ c = k_1.k_5 - k_2.k_4$$

In solving difference equations, a likely solution is tried and a general solution obtained by a process closely similar to that for differential equations. Equations 16 are treated by letting the solution be:

$$y_r = z^r,\ y_{r-1} = z^{r-1} \text{ etc.}$$

Substituting in equation 16,

$$a.z^{r+1} + b.z^r + c.z^{r-1} = 0 \tag{17}$$

The reason for such a change of variable is now apparent, for all of the series 16 reduce to the same quadratic,

$$a.z^2 + b.z + c = 0, \tag{18}$$

for which the roots are:

$$z_1 = \frac{-b + (b^2 - 4ac)^{½}}{2a} \tag{19}$$

and:

$$z_2 = \frac{-b - (b^2 - 4ac)^{½}}{2a}$$

The general solution of equation 16 is then:

$$y_r = \alpha z_1^r + \beta z_2^r \tag{20}$$

where α and β are constants derived from the first and second members of the series. Substituting in equation 19 the values of the constants a, b, c and using the relationship $m_1.m_2 = k_2.k_4$, z is obtained in terms of m_1, m_2, n_1, n_2. Reducing the cumbersome solutions of equation 19 by neglecting terms in n_1 and n_2 greater than of first order, we finally obtain:

$$z_1 = 1 - \frac{m_1n_2 + m_2n_1}{m_1 + m_2 + 2m_1m_2} \quad \text{and} \quad z_2 = \frac{1 - m_1m_2}{(1 + m_1)(1 + m_2)} \tag{21}$$

Values of α and β are found from equation 20 where $r = 1$ and $r = 2$ to be:

$$\alpha = \frac{z_2y_1 - y_2}{z_1(z_2 - z_1)} \quad \text{and} \quad \beta = \frac{z_1y_1 - y_2}{z_2(z_1 - z_2)} \tag{22}$$

Provided that at least one of m_1 and m_2 is appreciably different from zero, as in all practical cases, z_2 will be appreciably different from unity, whereas z_1 will be very nearly equal to unity. Hence when r is large, equation 20 becomes:

$$y_r = \frac{\{z_2 \cdot y_1 - y_2\} \cdot z_1^{r-1}}{z_2 - z_1} \tag{23}$$

The value of y_r is finally obtained in terms of the original symbols, A, B, σ, μ, λ or δ, by insertion of the values of y_1 y_2 in equation 23 from equations 1, 3, 6, etc. and of z_1, z_2 from equation 21, to give 23 in the form:

$$k_{p_{r_{bb}}}[Q_r] = \frac{\mu[B]\{X_a + X_b\}}{\sigma[A]^2 + 2[A][B] + \mu[B]^2} \cdot \left\{1 - \frac{\sigma[A]^2 n_1 + \mu[B]^2 n_2}{\sigma[A]^2 + 2[A][B] + \mu[B]^2}\right\}^{r-1} \tag{24}$$

Since z_1 almost equals unity, equation 24 can be converted into the exponential form:

$$k_{p_{r_{bb}}}[Q_r] = \frac{\mu[B]\{X_a + X_b\}}{\sigma[A]^2 + 2[A][B] + \mu[B]^2} \cdot \exp. -(r-1) \cdot \frac{\sigma[A]^2 . n_1 + \mu[B]^2 . n_2}{\sigma[A]^2 + 2[A][B] + \mu[B]^2} \tag{25}$$

Similarly:

$$k_{p_{r_{aa}}}[P_r] = \frac{\sigma[A]\{X_a + X_b\}}{\sigma[A]^2 + 2[A][B] + \mu[B]^2} \cdot \exp. -(r-1) \cdot \frac{\sigma[A]^2 n_1 + \mu[B]^2 n_2}{\sigma[A]^2 + 2[A][B] + \mu[B]^2} \tag{26}$$

As a cross-check on equation 25, from it we obtain:

$$\sum_1^{\infty} k_{p_{r_{ab}}}[P_r] = 1/\sigma \int_1^{\infty} k_{p_{r_{aa}}}[P_r] = \frac{\sigma[A]\{X_a + X_b\}}{\sigma[A]^2 n_1 + \mu[B]^2 n_2} \tag{27}$$

By inserting the appropriate n_1 and n_2, it is readily shown that equation 26 gives identically the expressions previously derived for these summations (reference (1), Table II).

Substituting equations 25 and 26 in 5, 7, 9, 10, 23, and 14 and dividing by the rate equation d [A] /dt and d [B] /dt given in Part I, we can in principle integrate the resultant cumbersome functions for the weight distribution at any stage in reaction. It is not possible to integrate these equations explicitly, as in certain cases for the one-component system. However, they can be integrated numerically in any particular case to give the molecular weight distribution during the reaction.

The time-distribution functions are of two classes; for monomer and spontaneous termination and disproportionation:

$$\frac{d[A_r]}{dt} = S.e^{-V(r-1)}, \quad \frac{d[B_r]}{dt} = T.e^{-V(r-1)} \tag{28}$$

and for combination:

$$\frac{d[M_r]}{dt} = (S + T)(r - 2).e^{-V(r-2)} \tag{29}$$

As described by Herington and Robertson (2) for the single monomer polymerization systems, the number-average distribution curves for the first class decrease continuously with increasing chain length, but for combination the term including r before the exponential gives a maximum in the distribution curve. The distribution curves are of similar shape to those illustrated by these authors.

WEIGHT AND NUMBER-AVERAGE CHAIN LENGTH

By definition:

$$\text{Number-Average Chain Length} = \frac{\sum_2^{\infty} r\{[A_r] + [B_r]\}}{\sum_2^{\infty}\{[A_r] + [B_r]\}} \quad \text{and}$$

$$\text{Weight-Average Chain Length} = \frac{\sum_2^{\infty} r^2\{[A_r] + [B_r]\}}{\sum_2^{\infty} r\{[A_r] + [B_r]\}} \tag{30}$$

Since $V \ll 1$, from equation 28 and 29:

$$\sum_1^{\infty} e^{-Vr} = 1/V, \quad \sum_1^{\infty} r.e^{-Vr} = 1/V^2, \quad \sum_1^{\infty} r^2.e^{-Vr} = 2/V^3 \tag{31}$$

From equations 30 and 31, we have instantaneously for class one:

$$\frac{\text{Weight-average chain length}}{\text{Number-average chain length}} = \frac{2}{1} \tag{32}$$

and instantaneously for combination:

$$\frac{\text{Weight-average chain length}}{\text{Number-average chain length}} = \frac{3}{2} \tag{33}$$

These ratios are the same as for the single monomer polymerizations. It is to be noted that here also, although the instantaneous ratios are always these integral constants, the over-all chain length from the time origin to the time when the reaction is stopped need not be 2/1 and 3/2, respectively. An exact analysis of the variation of these ratios with extent of reaction will here also provide a good test for the mechanism.

Number-Average Chain Length

The instantaneous chain length equals:

$$\frac{\text{Rate of consumption of monomer}}{\text{Rate of initiation}}$$

$$\frac{-d\left\{[A] + [B]\right\}/dt}{X_a + X_b} \qquad (34)$$

for class 1.

and:

$$= \frac{2.-d\left\{[A] + [B]\right\}/dt}{X_a + X_b}$$

for combination. Using equation 34, the expressions for the different modes of initiation and termination are obtained by substitution of the rate expressions given in Part I, Table III.

The over-all number averages are respectively for class 1 and combination:

$$\frac{[A_o] + [B_o] - [A] - [B]}{\int\left\{X_a + X_b\right\} dt} \text{ and } \frac{2\left\{[A_o] + [B_o] - [A] - [B]\right\}}{\int\left\{X_a + X_b\right\} dt} \qquad (35)$$

Weight-Average Chain Length

Results 35 can also be obtained from the foregoing general theory by equations 28 and 29, being another cross-check on the mathematical analysis. The method from the general theory is, however, of greater importance in furnishing an equally simple expression for the over-all weight average. This is also very useful in the case of single monomer polymerization, for up to the present there is no way of obtaining the over-all weight average except by summing to infinity the expressions involving the usually complex chain distribuiton function. The same result has been obtained from general principles and can be used to give directly the over-all weight average chain lengths in cases where intractable mathematics is encountered in the laborious calculations from the distribution function.

For class 1, from equation 28:

$$\frac{d\left\{[A_r] + [B_r]\right\}}{dt} = (S + T)e^{-V(r-1)}$$

where $V \ll 1$.

Hence:

$$\sum_2^\infty \left\{[A_r] + [B_r]\right\} = \int (S + T)/V.dt$$

Similarly:

$$\sum_2^\infty r\left\{[A_r] + [B_r]\right\} = (S + T)/V^2.dt$$

and:

$$\sum_{2}^{\infty} r^2 \left\{[A_r] + [B_r]\right\} = \int 2(S + T)/V^3 . dt$$

These integrals cannot be evaluated explicitly. There are, however, relationships between S,T, and V, and the rate equations which can be used to transform these integrals:

viz.:

$$(S + T) = (X_a + X_b).V$$

and:

$$1/V = \frac{-d\left\{[A] + [B]\right\}/dt}{X_a + X_b}$$

Thus, the over-all number-average chain length equals:

$$\frac{\int (S + T)/V^2 . dt}{\int (S + T)/V . dt}$$

$$= \frac{[A_0] + [B_0] - [A] - [B]}{\int \left\{X_a + X_b\right\} dt}$$

which is equation 35.

Similarly, the over-all weight average chain length equals:

$$\frac{2\int (S + T)/V^3 . dt}{\int (S + T)/V^2 . dt}$$

$$= \frac{2\int 1/\left\{X_a + X_b\right\} \left\{d([A] + [B])/dt\right\}^2 . dt}{[A_0] + [B_0] - [A] - [B]} \tag{36}$$

For class two (combination), similarly the over-all weight-average chain length equals:

$$\frac{3\int 1/\left\{X_a + X_b\right\} \left\{d([A] + [B])/dt\right\}^2 . dt}{[A_0] + [B_0] - [A] - [B]} \tag{37}$$

Thus, if initiation is known, say from inhibition experiments, the over-all weight-average chain length can be evaluated simply by numerical methods if the A - B - t curves are determined.

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Synopsis

An extension of the kinetic analysis of the generalized reaction mechanism for copolymerization given in Part I has been carried out to obtain the functions for molecular weight distribution and number- and weight-average molecular weights.

Résumé

L'analyse cinétique du mécanisme de réaction durant la copolymérisation, tel qu'il a eté indiqué dans la première partie, a été étendue afin d'obtenir les fonctions de répartition des poids moléculaires, ainsi que les poids moléculaires moyens, en nombre et en poids.

Zusammenfassung

Die kinetische Analyse des verallgemeinten Reaktionsmechanismus, die im ersten Teil gegeben wurde, wird ausgedehnt, um eine Funktion fuer die Molekulargewichtsverteilung sowie die Zahlen-und Gewichtsdurchschnitte des Molekulargewichtes zu erhalten.

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LETTER TO THE EDITORS

STABILITY OF CHLORINE-CONTAINING COPOLYMERS

Two years ago we had occasion to prepare several batches of copolymers of vinyl acetate/trans-dichloroethylene and vinyl acetate/trichloroethylene. The compositions chosen were near the "cross-over" points estimated from the data of Alfrey and Greenberg (1) (75 mole % vinyl acetate, 25 mole % trans-dichloroethylene; 75 mole % vinyl acetate, 25 mole % trichloroethylene).

We have observed an interesting phenomenon relating to the stabilities of these copolymers. After standing for 2 years in closed amber bottles, the vinyl acetate/trichloroethylene copolymers were found to be odorless white powders, apparently unchanged. The vinyl acetate/trans-dichloroethylene copolymers, stored under identical conditions, had decomposed to form dark red tars, smelling strongly of acetic acid.

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Pyrolysis of Polyisobutene (Vistanex), Polyisoprene, Polybutadiene, GR-S, and Polyethylene in a High Vacuum

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I. INTRODUCTION

The method of pyrolytic fractionation of polymers, in conjunction with mass spectrometer analysis of the more volatile fractions, has been described previously in the case of polystyrene (1). Briefly, this method consists in heating a 25 to 50 mg. sample of a polymer, spread as a thin film on a platinum tray, in a high vacuum at 300 to 500°C. The products of pyrolysis are: (a) a solid residue, (b) a waxlike fraction, volatile at the temperature of pyrolysis, but not volatile at room temperature, (c) a liquid fraction, volatile at room temperature and (d) a gaseous fraction, volatile at the temperature of liquid air or liquid nitrogen. The liquid and gaseous fractions are analyzed in the mass spectrometer, while the waxlike fraction is tested for its average molecular weight by a micro freezing point-lowering method. Pyrolytic fractionation has now been extended to the study of other hydrocarbon polymers covering polyisobutene (Vistanex), polyisoprene, polybutadiene, polyethylene and a copolymer, GR-S consisting of 75% butadiene and 25% styrene.

The mass spectrometer is a relatively new analytical tool and requires a preliminary investigation of mass spectra of all individual pure compounds in a mixture before it can be used with due calibration to analyze such a mixture. This imposes certain limitations on the study of polymers by way of mass spectrometric analysis of decomposition products of pyrolysis. The above polymers and copolymer were selected for this investigation with these limitations in view. However, mass spectral data are being accumulated at the present time in various laboratories and are being compiled by the National Bureau of Standards (2). These data are gradually broadening the scope of analysis in two directions, to include a greater number and variety of compounds and to extend the mass range so that compounds of higher molecular weight could be analyzed. It will, therefore, be possible in the future to apply the method of pyrolytic fractionation to polymers and copolymers of a more complicated structure and containing, in addition to carbon and hydrogen, also oxygen, nitrogen, sulfur, chlorine and other elements.

One object of this investigation was to find a relationship between the structural formulae of polymers and their refractoriness under the influence of heat. This in turn could serve as a clue to the chemical and physical properties of the polymers. To take a specific example, the effect of double bonds and their frequency in the macromolecular chain, also the size, frequency and distribution of side chains, on the number and size of fragments obtained in the pyrolysis, is one of the problems investigated here. Another object was to broaden the application of mass spectrometry to the identification and analysis of polymers in general. At the present stage of development, the mass spectrometer can be used to analyze masses a little over 100. It so happens that the most significant part in the mass spectrum of the volatile products of pyrolysis lies in this mass range, also that this part of the spectrum is characteristic of any given polymer so far studied. This leads to the possibility of using mass spectrometric analysis in conjunction with pyrolytic fractionation as a general method to identify polymers and to determine the extent of their purity.

With the extension of the range of mass spectrometric analysis to larger masses than 100, it will be possible to study the larger fragments obtained in the pyrolysis of polymers. This additional information will lead to a better understanding of the structure and to a greater refinement of the analysis of high-polymer substances.

II. REVIEW OF LITERATURE

Most of the work on pyrolysis of high polymers was done in the past on natural rubbers. Bolland and Orr (3) carried out pyrolysis of rubber in a vacuum at 220-270°. Staudinger and co-workers (4,5) employed temperatures of 300-400° and a pressure of 0.1-0.3 in one case and 1 atmosphere in another. Midgley and Henne (6) and Bassett and Williams (7) used temperatures of 600-700° and atmospheric pressure. In all this work the products of pyrolysis contained considerable amounts of isoprene and dipentene. As to pyrolysis of synthetic polymers, Seymour (8), employing temperatures of 150° to 500° and pressures of 0.5 mm. and 1 atmosphere, found that the order of thermal stability in the case of 3 polymers was: polyethylene > polystyrene > polyisobutene. Recently, Wall (9) pyrolyzed at 400° in a vacuum 1-mg. samples of rubber, polyethylene, polyisobutene, polystyrene, polyisoprene and other polymers and analyzed the products of pyrolysis in a mass spectrometer.

III. APPARATUS AND EXPERIMENTAL PROCEDURE

The same apparatus and experimental procedure as were used in the work on polystyrene, were used also in this work, but with some slight modifications. The modified apparatus is shown in Figure 1. It differs from the previous apparatus in that the large tapered ground joint between the pyrolysis still and the condenser has been replaced by a horizontal flanged joint. The upper flange of this joint is connected to an outer jacket around the condenser instead of directly to the condenser. This was done to avoid excessive cooling of the joint by the liquid nitrogen in the condenser. The thermocouple wires, instead of passing through the joint, pass this time through tubes attached to the side arm leading to the evacuating system. In this way ordinary vacuum grease could be used in the ground joint instead of hard wax which had to be melted with a flame. Another modification consisted in changing the distance between the pyrolysis tray and the condenser from 1.7 to 1.2 cm. In this way it was possible to collect more of the condensate on the liquid nitrogen condenser and less on the inner wall of the pyrolysis still.

Modification of the experimental procedure involved some changes in the fractionation and designation of the fractions. The nonvolatilized residue was collected and designated as fraction I as in the case of polystyrene pyrolysis. The waxlike fraction, volatile at the temperature of pyrolysis but not volatile at room temperature, was deposited as previously in two parts, a larger part on the liquid nitrogen-cooled condenser and a smaller part on the inner wall of the apparatus. The larger part was collected from the condenser and its weight determined directly while the weight of the smaller part was calculated by subtracting the sum of the other volatile fractions from the weight of the total pyrolyzed part. On the average, in all the experiments reported in this paper, that part of the waxlike fraction which collected on the condenser represented about 95% of the total waxlike fraction when the pyrolyzed part was only a few percent of the original sample; this dropped to about 74% when the pyrolyzed part reached 10% of the sample and stayed at this level all the way down to complete pyrolysis. The sum of the two parts of the waxlike fraction was designated as fraction II, without stating the amount of each part, as this was not deemed important. In case of the polystyrene work, the larger part of the waxlike fraction amounted, on the average, to 64% of the total and was designated as fraction II, while the smaller part, which deposited on the wall of the apparatus amounted to 36% and was designated as fraction IV.

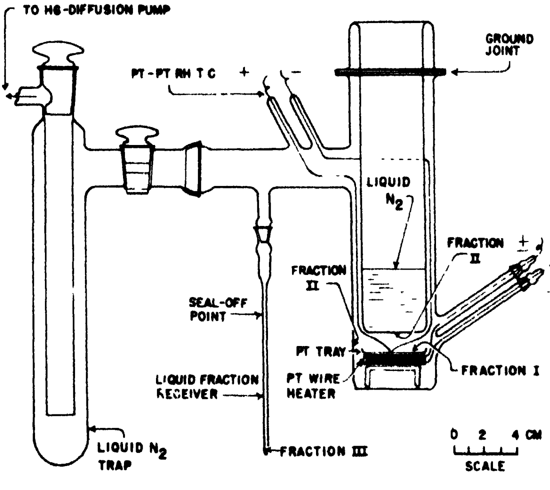


Fig. 1. Modified pyrolysis apparatus.

In collecting the liquid fraction III, the same procedure was followed as previously, except that in the case of polyisobutene, polybutadiene, GR-S and polyethylene this fraction was divided into a more volatile fraction IIIA and a less volatile one IIIB, in order to facilitate mass spectrometer analysis. However, in the case of polyisoprene mass spectrometer analysis could be carried out on fraction III in its entirety.

The gaseous fraction was collected in the same manner as in the previous work but was designated as fraction IV instead of V. This fraction consisted mainly of CH_4 mixed with some CO, CO_2 and air.

Only fractions IIIA (or III in the case of polyisoprene) and IV were analyzed in the mass spectrometer. Small amounts of air found in the gaseous fraction was most likely due to adsorption on the wall of the apparatus, the heater and the sample, or to its solution in the sample. Although most of this air was eliminated in the preliminary heating stage, as described in the previous paper, some of it was freed at the higher temperature. Small amounts of CO_2 and CO found in fraction IV could have come from the reaction of the polymer with adsorbed or dissolved oxygen or with oxygen present as a part of the polymer. The smaller the extent of pyrolysis in any given experiment, the greater the proportion of the impurities in fraction IV and, in cases where the pyrolyzed part was only a few percent of the original sample the gaseous fraction consisted almost entirely of CO_2, CO and air.

Some CO_2 was found in fractions III or IIIA in most of the experiments. Small amounts of solvents, such as benzene, ethanol, etc. also found their way into fraction III or IIIA of some of the experiments. These were undoubtedly due to adsorption. Here again the smaller the pyrolyzed part the more conspicuous were the impurities. The results of mass spectrometer analysis shown in this paper are based on calculations from which the impurities found in fractions III, IIIA or IV were excluded. In case of fractions III and IIIA the percentages of impurities are shown below the tables of analysis. In case of fraction IV, these impurities are not shown.

Fraction IIIB was not analyzed in the mass spectrometer because of the complexity of the spectrum and lack of spectra of the individual compounds it contained. No attempt was made to determine its average molecular weight by the micro freezing point-lowering method because this fraction was too small in the case of all polymers to make such a determination. Fraction II was analyzed for its average molecular weight by the micro freezing point-lowering method in cyclohexane, benzene or camphor. Some attempts were made to apply this method to the determination of the average molecular weight of the residue (fraction I), but the temperature drop was only a few tenths of a degree and the results were considered unreliable.

The micro freezing point-lowering method consisted in determining the average temperature between beginning of melting and collapse of the column of solidified solution contained in a sealed capillary tube. This method was tested on pure substances with the following results (the 3 figures following each compound in the order given stand for the molecular weight, as given by the empirical formulae, as determined by the micro method in benzene and as determined by the same method in cyclohexane): Decane, 142, 141, 125; 1-methylnaphthalene, 142, -, 125; Dodecane, 170, 174, 143; 2,2,4-Trimethyl-3-isopropyl-3-pentanol, 172, - , 153; Glycerol tripropionate, 260, - , 264; Dibutyl phthalate, 278, 268, 276; Glycerol tributyrate, 302, -, 305; Butyl phthalyl butyl glycolate, 336, - , 337. In the case of benzene as solvent, the results seem to be fairly close to the actual values. In the case of cyclohexane, the results are too low for some compounds for reasons that are not wholly apparent. Molecular weight of fraction II from polyethylene was determined in camphor by Rast's micro method (10).

IV. PYROLYSIS OF POLYISOBUTENE (VISTANEX)

The material used in these experiments was prepared by dissolving commercial Vistanex in benzene and precipitating with methanol. This was repeated twice and the methanol removed by evacuation. A 2% solution of the purified polyisobutene in benzene was used in the pyrolysis experiments. Experimental conditions and results of pyrolysis and fractionation are shown in Table I. Fifteen experiments were carried out at temperatures varying between 313° and 460°C. Weight of the sample varied from about 21 mg. to 60 mg. and in one case it was 82.9 mg. The solution of the polymer was spread on a platinum tray with an evaporating surface of about 12 sq. cm. The benzene was evaporated in a vacuum to a constant weight and a layer of the polymer 17-50 microns thick was thus obtained. After evacuation of the apparatus and a preliminary heating, as described in the previous paper, the temperature was raised from about 135° to the temperature of pyrolysis during 40-50 minutes, depending on the final temperature, a higher temperature requiring a longer time. The same procedure was followed in the case of the other polymers. The Vistanex as well as the other polymers formed in the tray a uniform layer with a glossy surface and it was difficult to observe at what temperature the polymer melted. Duration of pyrolysis at the maximum temperature was 30 minutes in all experiments with Vistanex.

TABLE I. Pyrolytic Fractionation of Polyisobutene (Vistanex)

Expt. No.	Wt. of sample, mg.	Temp., °C.	Duration, min.	Fractions in wt. per cent of original sample				Fraction III in per cent of total pyrolyzed part
				I Residue	II Non-vol. at room temp.	III Vol. at room temp.	IV Gaseous fraction	
1	24.9	313	30	97.2	2.4	0.4	0	14.2
2	22.5	344	30	83.0	11.3	5.7	trace	33.5
3	56.7	361	30	64.3	25.3	10.3	0.07	28.9
4	58.0	362	30	65.2	24.3	10.4	0.08	29.9
5	45.4	378	30	20.7	52.4	26.8	0.12	33.8
6	52.7	401	30	0.2	68.5	31.1	0.20	31.2
7	82.9	401	30	0.3	79.3	20.2	0.22	20.3
8	49.2	401	30	0.1	69.4	30.3	0.19	30.3
9	49.6	402	30	0.4	68.4	31.0	0.22	31.1
10	48.9	402	30	0.5	70.8	28.5	0.23	28.6
11	23.2	407	30	0.4	66.6	32.8	0.22	32.9
12	55.2	415	30	0.3	68.9	30.5	0.25	30.6
13	60.0	418	30	0.1	69.0	30.7	0.22	30.7
14	20.9	450	30	0.2	64.7	34.9	0.22	34.9
15	45.4	460	30	0.0	67.0	32.8	0.22	32.8

Average fraction III in per cent of total pyrolyzed part for all experiments, except Nos. 1 and 7................31.5 ± 0.8

It can be seen from Table I that thermal decomposition, under the experimental conditions employed, begins at 300° and is almost complete at 400°. At higher temperatures, decomposition was undoubtedly complete before the 30 minutes were over. The purpose of employing temperatures above 400° was to see what effect a faster rate of decomposition will have on the nature and relative amounts of the fractions. In the last column of Table I the yield of the liquid fraction III is shown in percent of total pyrolyzed part. In Expt. 1 the liquid fraction weighed about 0.1 mg. Since the accuracy of weighing on the semi-micro balance was about 0.05 mg., the accuracy of weighing 0.1 mg. was very low. In Expt. 7 the original sample was too large, weighing 82.9 mg., and spattering from the tray during pyrolysis was observed. This spattering resulted in an increase in fraction II and decrease in fraction III. The yield of fraction III in all the other experiments was practically constant, the average being 31.5 ± 0.8%.

Mass spectrometer analysis of the gaseous fraction IV was made for Expts. 4,6,8,10 and 12. The analysis showed the presence, in addition to CH_4, of small amounts of CO, H_2, O_2 and traces of CO_2. The yield of fraction IV in percent of the original sample was calculated for Expts. 4,6,8,10 and 12 on the basis of volume, pressure and mass spectrometer analysis, after excluding all the gaseous constituents, except CH_4. Yields of CH_4 for the other experiments were interpolated from those determined experimentally. In percent of total pyrolyzed part the yield of CH_4 for Expts. 4,6,8,10, and 12 is practically constant, the average being 0.22. Since the yields of the liquid and gaseous fractions are both constant, the yield of the waxlike fraction, which is obtained by subtracting the sum of the other two fractions from 100, is also constant and is equal on the average to 68.3% of the total pyrolyzed part.

In attempting to analyze fraction III in the mass spectrometer, it was found that the heavier constituents, consisting of 8 or more carbons, interfered with the analysis of the lighter constituents. According to a table compiled by Stull (11), the temperatures at which paraffins, monoolefins and diolefins have a vapor pressure of 1 mm., are: 1,3-pentadiene -71.8°, n-pentane -76.6°, 1-hexene -57.5°, n-hexane -53.9°, 2-heptene -35.8°, n-heptane -34.0°, 2-methyl-2-heptene -16.1° and n-octane -14°C. In view of this it would be possible to separate compounds consisting of 8 or more carbons at a temperature, near that of Dry Ice. This was accomplished in the following manner. Fraction III was first collected in a long sealed tube, 1.7 mm. inside diameter and 25-30 cm. long. By immersing one end of the tube in liquid nitrogen the fraction was concentrated at that end and the tube was bent in the center, by means of a flame, in the form of a U. The cold end was then removed from the liquid nitrogen and placed in a Dry Ice-acetone mixture at -75° and the other end immersed in liquid nitrogen. Distillation was continued for 3 minutes. In this way the less volatile compounds remained in the end of the tube at -75° while the more volatile ones collected at the other end. The tube was then melted at the center and the two fractions separated, the heavier one as fraction IIIB and the lighter one as fraction IIIA. In all cases the distribution between IIIA and IIIB was about 70 and 30% of the total fraction III. Since the total yield of fraction III was 31.5%, the yields of IIIA and IIIB were, on the average, 22.05 and 9.5% respectively.

Mass spectrometer analyses of fraction IIIA are shown in Table II for 7 experiments. Most of fraction IIIA consists of isobutene, the average being 92.2 mole percent. The next significant constituent, neopentane, amounts to 6% on the average. In addition to these there is 1.6% isobutane and 0.2% pentenes. The last column of Table II shows the average yield of components in percent of total pyrolyzed part. The yield of the monomer, isobutene, according to this table is 20.18%.

TABLE II. Mass Spectrometer Analysis of Fraction IIIA Obtained in the Pyrolysis of Polyisobutene

Expt. No. .... Temp. of pyrolysis °C. . Part pyrolyzed in %		3 361 35.7	4 362 34.8	7 401 99.7	9 402 99.6	10 402 99.5	12 415 99.6	13 420 99.9	Average for all experiments	Average component in % of total pyrolyzed part
Component	Mole. wt.	In Mole per cent								Weight %
Isobutene	56.1	90.3	89.6	93.9	92.7	93.0	93.0	92.8	92.2	20.180
Isobutane	58.1	1.4	1.3	1.9	1.5	1.6	1.6	1.7	1.6	0.320
Pentenes	70.1	0.5	0.7	-	0.4	-	-	0.2	0.2	0.048
Neopentane	72.1	7.8	8.4	4.2	5.4	5.4	5.4	5.3	6.0	1.502
Total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	22.050
CO_2	44	Trace	Trace	Trace	Trace	Trace	Trace	Trace		

No mass spectrometer analyses were made of fractions IIIB for the reasons explained above. Judging from the fact that fraction IIIA consisted mainly of the monomer and that fraction IIIB was not volatile at -75, but was volatile at room temperature, it can be assumed that the latter fraction consisted of the dimer and trimer.

Fraction II was soluble in cold benzene or cyclohexane. The results of 5 molecular weight determinations are shown in Table III, the average being 543. In making these determinations, an ordinary thermometer, having 3 degrees centigrade per 1 cm. length and carrying 0.2 degree divisions, was used. On the same consideration as in the case of fraction IIIB, fraction II most likely contained polymeric fragments consisting on the average of 9-10 monomers. The residue (fraction I) was soluble in cold benzene or cyclohexane. No molecular weight determinations were made of this fraction.

TABLE III. Average Molecular Weight of Waxlike Fraction (II) Obtained in the Pyrolysis of Polyisobutene

Expt. No.	Temp. of pyrolysis, °C.	Part pyrolyzed, %	Freezing point lowering of C_6H_{12}, °C.	Average molecular weight
3	361	35.7	1.25	507
4	362	34.8	1.90	518
6	401	99.8	2.43	506
8	401	99.9	2.50	612
9	402	99.6	1.60	570
Average				543

V. PYROLYSIS OF POLYISOPRENE

A 27 g. sample of commercial polyisoprene was extracted 3 times with 300 ml. portions of ethanol-toluene azeotrope. The sample was stored, wet with the azeotrope, under benzene. A dilute solution of the purified material in benzene was used in the pyrolysis experiments. Results of 13 experiments are shown in Table IV. It appears from this table that pyrolysis begins at 300° and is almost complete at 400°. On the whole polyisoprene decomposes more readily than polyisobutene. Except for Expts. 1,2 and 3 at low temperatures, the yield of fraction III is fairly constant and is equal on the average to 11.3 ± 0.4% of the total pyrolyzed part. The yield of fraction IV was obtained from mass spectrometer analysis for Expts. 1,2,4,5,7,11 and 13. Yields for the other experiments were obtained by interpolation. The average yield in percent of total pyrolyzed part is 0.016. The average yield of fraction II is therefore 100 - (11.3 + 0.016) = 88.7%.

In analyzing fraction III in the mass spectrometer, it was found that the heavier components, consisting of 8 or more carbons, did not interfere with the analysis of the lighter components. In view of this, fraction III was not divided into fractions IIIA and IIIB, but was analyzed directly. Results of mass spectrometer analyses of fraction III for 9 experiments are shown in Table V. These analyses show the presence in this fraction of small amounts of ethanol, acetone, methyl ethyl ketone, benzene, toluene and CO_2. In experiments 1 and 2, where the total pyrolyzed part was only 2.4% and 3.0%, respectively, the relative amounts of impurities due to adsorbed and dissolved gases and liquids appear exaggerated. Considering Expts. 4 to 13 we can see from Table V that the most abundant constituent of fraction III is isoprene amounting on the average to 90.8 mole percent. Next in abundance are the pentenes 4.6%, cyclopentadienes 1.5%, butenes 1.2% and hexadienes 1%.

TABLE IV. Pyrolytic Fractionation of Polyisoprene

				Fractions in wt. per cent of original sample				
Expt. No.	Wt. of sample, mg.	Temp., °C.	Duration, min.	I Residue	II Non-vol. at room temp.	III Vol. at room temp.	IV Gaseous fraction	Fraction III in per cent of total pyrolyzed part
1	56.8	302	30	97.6	2.0	0.4	0	16.7
2	49.8	302	30	97.0	2.5	0.5	trace	16.7
3	51.3	325	30	89.9	7.9	2.2	trace	21.8
4	50.6	352	30	51.5	43.0	5.5	0.005	11.3
5	53.0	354	30	45.8	49.7	4.5	0.006	8.3
6	52.5	354	60	21.1	70.0	8.9	0.012	11.3
7	57.0	354	90	20.0	70.0	10.0	0.014	12.5
8	51.8	380	30	16.6	73.9	9.5	0.014	11.4
9	44.1	380	30	8.9	81.5	9.6	0.014	11.5
10	52.6	380	30	8.7	80.7	10.6	0.014	11.6
11	49.5	400	30	5.4	83.3	11.3	0.020	11.9
12	56.5	403	30	3.7	84.6	11.7	0.021	12.2
13	58.6	405	30	3.8	84.6	11.6	0.025	12.1

Average fraction III in per cent of total pyrolyzed part for Expts. 4 to 13, inclusive .... 11.3 ± 0.4

Dipentene, which is the dimer of isoprene, showed up in the mass spectra of fraction III of Expts. 1 and 2, but not in those of the other experiments. Dipentene has a vapor pressure of 1 mm. at 14° and 5 mm. at 40.4° (11). Since fraction III was collected at room temperature it contained all the dipentene formed in the pyrolysis. On the other hand the trimer, consisting of 15 carbons would have too low a vapor pressure to distill into fraction III at room temperature. In view of this, it can be assumed that fraction III contained, in addition to the compounds shown in Table V, also a considerable amount of dipentene. In experiments 1 and 2, where the total weight of fraction III was small, the partial vapor pressure of dipentene was sufficiently large to show its presence in appreciable amounts. In the other experiments the large amount of a volatile compound such as isoprene suppressed the vapor pressure of dipentene, so that the latter did not show up in the spectrum. Fraction III from Expt. 8 was expanded into a large volume in a specially designed apparatus described previously (1) and an expanded sample analyzed in the mass spectrometer. Peaks indicating the presence of a large amount of dipentene appeared in the spectrogram, but no quantitative data could be obtained as to its relative amount.

TABLE V. Mass Spectrometer Analysis of Liquid Fraction (III) Obtained in the Pyrolysis of Polyisoprene

Expt. No.		1	2	4	5	6	7	10	12	13	Av. 4 to 13 incl.	Av. component in % of total pyrolyzed part
Temp. of pyrolysis °C		302	302	352	354	354	354	380	403	405		
Part pyrolyzed in %		2.4	3.0	48.5	54.2	78.9	80.0	91.3	96.3	96.2		
Component	Mol. Wt.	In Mole per cent										Weight %
Butenes	56.1	4.5	2.4	0.9	0.9	1.1	1.2	0.8	1.2	1.2	1.1	0.051
Cyclopentadienes	66.0	1.9	2.4	2.1	1.8	-	1.4	1.2	1.5	2.4	1.5	0.081
Isoprene	68.1	60.0	72.2	91.6	91.2	92.0	89.4	91.2	90.6	89.8	90.8	5.150
Pentenes	70.1	4.3	2.6	3.5	3.6	4.6	5.5	5.2	5.0	4.9	4.6	0.277
Cyclohexadienes	80.1	0.6	0.8	0.3	0.1	0.3	0.5	0.3	0.3	0.3	0.3	0.020
Hexadienes	82.1	3.5	3.0	1.0	1.4	1.2	1.2	0.8	0.8	0.7	1.0	0.068
Hexenes	84.1	0.6	0.8	0.1	0.1	0.2	0.2	0.1	0.2	0.2	0.1	0.007
Cycloheptadienes	94.1	1.4	1.7	0.2	0.3	0.2	0.3	0.2	0.1	0.1	0.2	0.015
Heptadienes	96.1	1.2	1.3	0.3	0.4	0.3	0.3	0.2	0.2	0.2	0.3	0.023
Heptenes	98.1	12.9	1.8	-	0.1	-	0.1	-	0.1	0.2	0.1	0.008
Dipentene	136.1	9.1	11.0	-	0.1	0.1	-	-	-	-	-	-
Totals		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	5.700
Mole per cent Impurities in Original Analysis												
Ethanol	46.0	6.9	8.5	0.2	0.5	0.5	0.5	0.2	0.2	-		
Acetone	58.0	2.5	3.2	0.5	0.7	0.5	0.5	0.3	0.3	0.3		
MEK*	72.1	1.4	2.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1		
Benzene	78.0	1.1	4.7	0.2	0.1	0.1	0.2	-	-	-		
Toluene	92.1	0.3	0.3	-	-	-	-	-	-	-		
CO_2	46.0	38.6	27.6	7.2	19.0	4.8	4.4	3.4	5.6	3.9		

*Methyl ethyl ketone

In order to estimate the yield of dipentene in fraction III, this fraction in the case of experiments 8,9 and 11 was divided into IIIA and IIIB, by a procedure described above, and the two parts weighed on the semi-micro balance. The distribution between the two parts was 5.7 and 5.6% in IIIA and IIIB, respectively. On this basis the yield of isoprene is 5.15% of the total pyrolyzed part, as shown in the last column of Table V. It is not likely that fraction IIIB contained much of the trimer of isoprene. The trimer contains 15 carbons and a compound of similar molecular weight, for example, pentadecane, $C_{10}H_{22}$, has a vapor pressure of 1 mm. at 91.6°. On this consideration, the yield of dipentene was about 5.6% of the total pyrolyzed part. Whether the ratio of yields of isoprene to dipentene varies with temperature of pyrolysis and if so, in what direction, is not clear from this investigation.

TABLE VI. Average Molecular Weight of Waxlike Fraction (II) Obtained in the Pyrolysis of Polyisoprene

Expt. No.	Temp. of pyrolysis, °C.	Part pyrolyzed, %	Freezing point lowering of C_6H_{12}, °C.	Average molecular weight
4	352	48.5	2.70	610
6	354	78.9	3.45	542
7	354	80.0	3.10	572
12	403	96.3	2.90	578
13	405	96.2	2.25	581
Average				577

The waxlike fraction (II) was soluble in cold benzene or cold cyclohexane. The results of molecular weight determinations in cyclohexane are shown in Table VI. The average of 5 determinations is 577, which means that on the average the fragments in this fraction consisted of about 8-9 monomer units. The residue, fraction I, was also soluble in cold benzene or cold cyclohexane, but no molecular weight determinations were made of this fraction.

VI. PYROLYSIS OF POLYBUTADIENE

A sample of polybutadiene was purified by dissolving in benzene and precipitating with methanol. This operation was repeated several times and finally the sample, freed from methanol was dissolved in benzene to make a dilute solution. Results of 12 pyrolysis experiments are shown in Table VII. As seen from this table, polybutadiene is more refractory than polyisobutene, polyisoprene or polystyrene, when heated under similar conditions. This polymer begins to break up at about 350° and decomposition is almost complete at 477°. The yield of fraction III in percent of total pyrolyzed part, stays fairly constant, on the average at 14.0 ± 1.0%, up to a temperature of pyrolysis of 400-425°. Above this temperature the yield drops to a small fraction of the above value as indicated in the last column of Table VII. The yield of the gaseous fraction (IV), on the contrary, stays constant at 0.30% of the total pyrolyzed part throughout the entire temperature range.

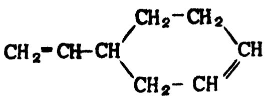
TABLE VII. Pyrolytic Fractionation of Polybutadiene

				Fractions in wt. per cent of original sample				
Expt. No.	Wt. of sample, mg.	Temp., °C.	Duration, min.	I Residue	II Non-vol. at room temp.	III Vol. at room temp.	IV Gaseous fraction	Fraction III in per cent total pyrolyzed part
1	49.9	350	30	93.9	5.3	0.8	trace	13.1
2	63.6	351	30	93.2	6.0	0.8	trace	11.8
3	54.4	400	30	81.5	15.5	3.0	trace	16.2
4	50.3	400	30	80.2	17.2	2.5	0.06	12.6
5	51.3	401	60	76.9	19.0	4.0	0.08	17.3
6	50.1	401	120	67.4	27.5	5.0	0.11	15.3
7	50.7	425	30	53.7	40.7	5.5	0.12	11.8
8	31.2	450	30	19.4	72.1	8.3	0.23	10.3
9	52.7	450	30	14.4	78.7	6.6	0.25	7.7
10	50.3	450	30	13.7	81.1	5.0	0.23	5.8
11	40.4	477	30	0.9	92.5	6.3	0.28	6.4
12	51.1	500	30	0.3	97.2	2.2	0.30	2.2

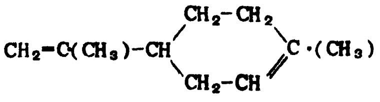
Average fraction III in per cent of total pyrolyzed part for Expts. 1 to 7 inclusive........................ 14.0 ±1.0

Fraction III was divided into fractions IIIA and IIIB volatile at -75° and room temperature and amounting to 4.2% and 9.8% of the total pyrolyzed part, respectively. Mass spectrometer analyses of fraction IIIA are shown for 9 experiments in Table VIII. These experiments cover the entire range of pyrolysis from 6.1% to almost 100% decomposition. A gradual decrease in the content of 1,3-butadiene, the principal constituent of fraction IIIA, and a corresponding increase in the content of most of the other constituents of this fraction, with rise in temperature of pyrolysis or extent of pyrolysis, is noted. On the other hand, butene, the second largest constituent, passes through a maximum at 20-30% decomposition. Yields of the various components in percent of total pyrolyzed part are shown in the last column of Table 8 for Expt. 5 which seems to have approximately the average composition of fraction IIIA. Yield of the monomer, 1,3-butadiene, in Expt. 5 is 1.515%; however, considering other experiments, the yield varies from 2.27% for Expt. 1 to 0.67% for Expt. 9.

Fraction IIIB could not be analyzed in the mass spectrometer and no determination was made of its average molecular weight. On the basis of the same arguments given in the case of polyisoprene, this fraction most likely consists of the dimer of butadiene and in the form of vinyl cyclohexene, which is the analogue of dipentene:



vinyl cyclohexene



dipentene

The gaseous fraction (IV) was also analyzed in the mass spectrometer. As in the case of the other polymers, this fraction consisted

TABLE VIII. Mass Spectrometer Analysis of Fraction IIIA Obtained in the Pyrolysis of Polybutadiene

Expt. No.		1	3	4	5	6	7	9	10	12*	5
Temp. of pyrolysis, °C.		350	400	400	401	401	425	450	450	500	Components in % total pyrolyzed part
Part pyrolyzed in %		6.1	18.5	19.8	23.1	32.6	46.3	85.6	86.3	99.7	
Component	Mol. wt.	In Mole per cent									Wt. %
Ethylene	28.0	-	4.9	6.0	7.3	7.5	11.6	8.4	11.7	13.0	0.166
Ethane	30.0	0.8	5.0	5.1	8.5	11.1	14.6	18.5	16.5	17.2	0.208
Propadiene	40.0	-	-	-	1.0	0.9	-	0.8	-	1.2	0.032
Propylene	42.0	3.8	9.2	9.3	5.8	8.1	16.8	14.6	14.9	9.4	0.198
Propane	44.0	0.9	1.3	1.5	4.2	5.8	5.4	9.8	8.0	7.7	0.151
1,3-Butadiene	54.1	58.9	40.9	42.2	34.4	26.7	28.2	13.2	20.7	22.1	1.515
Butenes	56.1	11.7	21.3	19.3	26.1	26.1	14.5	23.6	16.5	12.4	1.190
Butanes	58.1	1.0	2.2	2.0	2.9	3.9	4.0	6.1	5.1	5.1	0.138
Cyclopentadienes	66.1	2.5	1.6	1.3	0.7	0.4	0.4	0.1	0.3	0.4	0.037
Pentadienes	68.1	8.5	6.2	6.1	4.2	3.3	1.2	1.0	1.6	3.1	0.233
Pentenes	70.1	1.0	3.5	3.1	3.4	3.3	2.1	2.4	3.0	3.2	0.194
Pentanes	72.1	-	1.0	1.1	1.5	1.6	1.2	1.5	1.7	1.7	0.088
Cyclohexadienes	80.1	3.6	0.4	0.5	-	-	-	-	-	-	-
Hexadienes	82.1	7.2	2.2	2.3	-	1.1	-	-	-	0.3	-
Hexenes	84.1	0.1	0.2	0.2	-	0.1	-	-	-	0.4	-
Total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	97.2	4.15
CO	28	-	-	-	-	-	-	-	6.3	-	
CO_2	44	21.2	8.8	8.5	0.5	-	0.3	0.2	-	0.7	

*In addition to the components indicated here, there were also 1.4% heptadienes and 1.4% vinylcyclohexene.

chiefly of CH_4 mixed with some CO, N_2, O_2 and CO_2. Actual analyses of this fraction were made for Expts. 1,4,5,6,9 and 10. Values for the experiments were interpolated from the experimental values. Yield of CH_4 in percent of total pyrolyzed part is fairly constant and is equal on the average to 0.29% of the total pyrolyzed part.

The waxlike fraction (II) was soluble in benzene, but not in cyclohexane. Molecular weight determination of this fraction by the micro freezing point-lowering method was, therefore, carried out in benzene. The results are given in Table IX. The average of 6 determinations is 739, signifying that the average fragment in fraction II consisted of about 13-14 monomers. The residue was not soluble either in benzene or cyclohexane.

TABLE IX. Average Molecular Weight of Waxlike Fraction (II) Obtained in the Pyrolysis of Polybutadiene

Expt. No.	Temp. of pyrolysis, °C.	Part pyrolyzed, %	Freezing point lowering of C_6H_6, °C.	Average molecular weight
5*	401	23.1	0.55	700
6	401	32.6		
7	425	46.3	0.60	666
8	450	80.6	0.48	788
9	450	85.6	0.30	772
10	450	86.3	0.67	726
11	477	99.1	0.60	784
Average				739

*Molecular weight determination was made on the combined fractions II from Expts. 5 and 6.

The peculiar behavior of polybutadiene in giving on pyrolysis lower yields of fraction III at temperatures above 425°, is undoubtedly due to spattering which was observed to take place when the tray was heated too fast. In this case incompletely pyrolyzed material reached the condenser. As a result the yield of fraction III was reduced and fraction II acquired a higher average molecular weight. Turning back to Table IX, we see that the molecular weight of fraction II is greater for temperatures of 450° or above than for temperature below 450°. In the case of polyisobutene, in Expts. 14 and 15, Table I, the temperature of pyrolysis was 450° and 460° respectively, but no spattering occurred because most of the material was pyrolyzed before these temperatures were reached.

VII. PYROLYSIS OF GR-S

GR-S, consisting of 75% butadiene and 25% styrene, was dissolved in benzene and precipitated with methanol. This was repeated several times and the precipitate freed from methanol and dissolved in benzene. Results of pyrolysis and fractionation of 9 samples are shown in Table X. Here, as was the case with polybutadiene, the yield of fraction III stays constant at lower temperatures, then drops at 426° or above. The average of the constant for the first 5 experiments is 11.8 ± 0.4% of the total pyrolyzed part. Fraction III was separated into fractions

IIIA, yield 3.9%, and IIIB, yield 7.9%. Mass spectrometer analyses of fraction IIIA for all 9 experiments are shown in Table XI. These analyses resemble very closely those obtained for fractions IIIA from polybutadiene. Apparently, styrene and toluene, which are decomposition products in the pyrolysis of polystyrene (1), were retained in fraction IIIB, due to their low vapor pressure at -75°. According to Stull's table (11), the temperatures at which styrene and toluene have a vapor pressure of 1 mm. are -7 and -26.7° respectively. In GR-S pyrolysis, as in the case of polybutadiene, the content of 1,3-butadiene drops and that of most of the other significant constituents of fraction IIIA rises with rise in temperature. Composition of fraction IIIA in percent of total pyrolyzed part is shown in the last column for Expt. 5 which seems to have about the average percentage of components for all the experiments. The yield of butadiene, according to this table, is 1.906% for Expt. 5. Considering the other experiments, this yield varies from 2.14% for Expt. 1 to 1.71% for Expt. 9. Although in the case of pyrolysis of polystyrene, fraction III, which consists mostly of styrene, could be analyzed in the mass spectrometer, fraction IIIB from pyrolysis of GR-S could not be similarly analyzed, because of the complexity of the spectrum arising from the presence in this fraction of the dimer of butadiene, presumably vinyl cyclohexene.

TABLE X. Pyrolytic Fractionation of GR-S

Expt. No.	Wt. of sample, mg.	Temp., °C.	Duration, min.	Fractions in wt. per cent of original sample				Fraction III in per cent total pyrolyzed part
				I Residue	II Non-vol. at room temp.	III Vol. at room temp.	IV Gaseous fraction	
1	52.7	352	30	93.1	6.1	0.8	Trace	11.6
2	45.4	375	30	80.1	17.8	2.0	0.05	10.0
3	46.3	375	30	62.2	32.9	4.8	0.10	12.7
4	41.0	400	30	44.5	48.3	7.1	0.13	12.8
5	44.7	400	30	43.5	49.6	6.8	0.12	12.0
6	59.3	426	30	28.3	65.3	6.2	0.15	8.7
7	51.6	450	30	5.4	87.4	7.0	0.16	7.4
8	46.5	450	30	0.3	93.6	5.9	0.17	5.9
9	47.8	455	30	0.4	92.7	6.7	0.17	6.7

Average of fraction III in per cent of total pyrolyzed part for experiments 1 to 5 inclusive.......... ...... 11.8 ± 0.4

The gaseous fraction was analyzed in the mass spectrometer only for Expts. 2,4,5 and 9. The other values were interpolated from those determined experimentally. The results are shown in Table X. The average yield of CH_4 is 0.19%. Fraction II was only slightly soluble in cyclohexane, but soluble in benzene. Results of molecular weight determinations for 4 experiments are shown in Table XII. The average molecular weight is 712, corresponding approximately to a composition of 8-9 units of butadiene and 3 units of styrene per fragment. Fraction I was soluble in cold or hot benzene, but not in cyclohexane, cold or hot.

TABLE XI. Mass Spectrometer Analysis of Fraction IIIA Obtained in the Pyrolysis of GR-S

Expt. No.		1	2	3	4	5	6	7	8	9	5 Components in % total pyrolyzed part
Temp. of pyrolysis °C		352	375	375	400	400	426	450	450	455	
Part pyrolyzed in %		6.9	19.9	37.8	55.5	56.6	71.7	94.6	99.7	99.6	
Component	Mol. wt.	In Mole per cent									Wt. %
Ethylene	28.0	3.5	4.8	8.1	11.1	11.5	11.4	12.6	12.6	10.9	.266
Ethane	30.0	1.4	1.8	6.0	9.8	10.6	10.0	11.3	12.7	12.0	.263
Propadiene	40.0	0.4	0.2	0.2	0.5	0.4	0.7	0.8	-	0.8	.013
Propylene	42.0	0.4	1.8	8.3	7.9	9.9	4.7	4.9	10.4	9.1	.344
Propane	44.0	1.7	2.2	2.7	4.4	4.9	4.2	5.8	4.5	5.7	.177
1,3-Butadiene	54.1	63.3	63.9	57.7	43.8	42.6	43.9	36.6	38.5	38.6	1.906
Butenes	56.1	8.8	11.1	13.5	13.6	13.8	16.1	15.6	13.0	12.7	.634
Butanes	58.1	3.3	1.3	1.5	3.2	2.8	2.6	3.1	3.5	3.7	.134
Cyclopentadienes	66.1	1.7	1.5	0.1	0.3	0.2	0.5	0.7	0.2	0.3	.011
Pentadienes	68.1	6.7	7.0	0.9	2.6	1.2	2.3	3.5	1.7	2.4	.058
Pentenes	70.1	1.0	1.2	0.7	1.8	1.2	2.4	3.1	1.6	2.2	.069
Pentanes	72.1	-	-	0.3	1.0	0.9	0.9	1.1	1.3	1.4	.054
1,3-Cyclohexadienes	80.1	4.5	1.4	-	-	-	-	0.2	-	-	-
Hexadienes	82.1	3.0	1.6	-	-	-	0.2	0.5	-	0.1	-
Hexenes	84.1	0.3	0.2	-	-	-	0.1	0.2	-	0.1	-
Totals		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	3.930
CO_2	44	29.0	9.1	9.9	12.8	7.9	0.2	-	6.0	7.8	
Benzene	-	0.4	0.2	-	-	-	-	-	-	-	

TABLE XII. Average Molecular Weight of the Waxlike Fraction (II) Obtained in the Pyrolysis of GR-S

Expt. No.	Temp. of pyrolysis, °C.	Part pyrolyzed, %	Freezing point lowering of C_6H_6, °C.	Average molecular weight
3	375	37.8	0.60	707
5	400	56.6	0.60	726
6	426	71.7	0.57	687
7	450	94.6	0.50	728
Average...........................				712

VIII. PYROLYSIS OF POLYETHYLENE

The polyethylene used in this investigation was a pure grade polymer having an average molecular weight of about 20,000. It could not be dissolved in the ordinary solvents and was used in the form of a suspension in benzene. Polyethylene proved very resistant to thermal decomposition. Pyrolysis started at 360° and was almost complete at 475°. The results of 13 experiments are shown in Table XIII. Here the yield of fraction III was very small, the average being 3.4 ± 0.5% of the total pyrolyzed part. There is a considerable variation from this average in the individual experiments, but this is to be expected in view of the fact that the weight of the liquid fraction was only 0.25 to 1.5 mg. and the accuracy of weighing was not better than 0.05 mg. Duration of experiments of maximum temperatures varied from 30 to 90 minutes.

Fraction III was divided into fractions IIIA and IIIB in the manner described above. Mass spectrometer analyses of fraction IIIA for 4 experiments are shown in Table XIV. Polyethylene is unique

TABLE XIII. Pyrolytic Fractionation of Polyethylene

Expt. No.	Wt. of sample, mg.	Temp., °C.	Duration, min.	Fractions in wt. per cent of original sample				Fraction III in per cent of total pyrolyzed part
				I Residue	II Non-vol. at room temp.	III Vol. at room temp.	IV Gaseous fraction	
1	54.3	360	30	98.6	1.3	0.1	Trace	7.1
2	71.9	400	60	87.8	11.6	0.6	Trace	4.9
3	54.5	401	30	85.2	13.9	0.9	Trace	6.1
4	56.6	405	30	76.5	23.1	0.4	Trace	1.7
5	67.2	405	60	83.0	16.3	0.7	Trace	4.1
6	57.6	405	30	82.4	16.8	0.8	Trace	4.2
7	57.6	405	90	78.9	20.6	0.5	Trace	2.4
8	65.5	429	30	29.7	67.9	2.4	Trace	3.4
9	59.1	429	30	37.3	61.6	1.1	Trace	1.8
10	56.0	430	60	29.4	68.4	2.2	Trace	3.1
11	59.9	431	60	11.4	86.1	2.5	Trace	2.8
12	64.6	431	90	6.1	91.3	2.6	Trace	2.8
13	36.4	475	30	1.4	95.5	3.1	Trace	3.1

Average fraction III in per cent of total pyrolyzed part for all experiments except 1... .... 3.4 ± 0.5

in the sense that the macro-molecular chain is devoid of any marks indicating the monomeric units from which it is built. Thermal decomposition, according to Table IV, seems to follow a random pattern giving rise mostly to straight chain paraffins and monoolefins. It is likely that fractions IIIB and II consist of the same types of molecules, except that they are longer. The 4 analyses shown in Table XIV resemble each other very closely in spite of the fact that the temperature of pyrolysis varied from 405° to 475° and the extent of decomposition varied from 23.5% to almost 100%. The average composition of fraction III in percent of total pyrolyzed part is shown in the last column of Table XIV.

TABLE XIV. Mass Spectrometer Analysis of Fraction IIIA Obtained in the Pyrolysis of Polyethylene

Expt. No.		4	9	10	13	Av. of Expts. 4 to 13 inclusive	Av. component in % of total pyrolyzed part
Temp. of pyrolysis, °C.		405	429	430	475		
Part pyrolyzed in %		23.5	62.7	70.6	98.6		
Component	Mol. wt.	In Mole per cent					Wt. %
Ethylene	28	4.8	4.0	4.1	4.2	4.3	0.025
Ethane	30	14.3	13.4	10.9	11.2	12.4	0.076
Propadiene	40	1.2	-	-	-	0.3	0.002
Propylene	42	-	3.7	10.8	6.1	5.2	0.045
Propane	44	15.3	10.3	16.2	17.5	14.8	0.136
Butenes	56.1	24.5	25.8	22.7	25.4	24.6	0.282
n-Butane	58.1	16.8	22.1	18.6	18.7	19.1	0.225
Pentadienes	68.1	-	0.3	0.4	0.9	0.4	0.005
Pentenes	70.1	8.3	8.4	6.7	6.7	7.5	0.108
n-Pentane	72.1	6.8	7.7	6.2	3.9	6.2	0.091
Hexadienes	82.1	0.8	0.3	-	-	0.3	0.005
Hexenes	84.1	3.5	2.7	2.4	4.1	3.2	0.056
n-Hexane	86.1	1.6	1.1	0.8	1.3	1.2	0.022
1-Heptene	98.1	0.5	0.1	0.2	-	0.2	0.004
n-Heptane	100.1	1.6	0.1	-	-	0.4	0.008
Total		100.0	100.0	100.0	100.0	100.0	1.1
CO_2	44	0.3	3.6	-	2.1	-	-

Fraction IIIB can be assumed to consist of paraffins and olefins containing 8 to 15 carbons in the chain. The gaseous fraction contained only a trace of CH_4. The waxlike fraction (II) was quite insoluble in cold benzene, although soluble in hot benzene. The average molecular weight of this fraction was determined by the micro freezing point-lowering method in camphor. The results are shown in Table XV. The amount of material in fraction II was too small in most experiments and it was found necessary in some cases to combine the yields from two experiments for a molecular weight determination. The average of 4 determinations was 692, corresponding to an average straight-chain fragment of about 50 carbons. The residue was a horny substance insoluble in cyclohexane or benzene, hot or cold.

TABLE XV. Average Molecular Weight of Waxlike Fraction (II) Obtained in the Pyrolysis Polyethylene

Expt. No.	Temp. of pyrolysis, °C.	Part pyrolyzed, %	Freezing pt. lowering of camphor	Average molecular weight
5	405	17.0	4.8	690
6	405	17.6		
8	429	70.3	5.4	691
10	430	70.6	5.0	687
11	431	88.6		
9	429	62.7	5.6	699
12	431	93.9		
Average				692

IX. DISCUSSION OF RESULTS

It was shown in the course of this investigation that fractionation of the volatile products of pyrolysis facilitates the analysis of the products whether by means of the mass spectrometer or by other means. One striking result of this investigation is that in the case of polyisobutene and polyisoprene the yield of the monomer is practically constant within a wide range of temperature, duration of experiment, amount of sample used or extent of pyrolysis. The same was found true in the pyrolysis of polystyrene (1). In the case of polybutadiene the yield of the monomer decreases markedly with the rise in temperature of pyrolysis. As to polyethylene, one cannot speak of a monomer because the macromolecular chain does not have any distinctive marks to indicate the unit from which it was built. Nevertheless, the relative amounts of small fragments up to about 8 carbons remain fairly constant through the temperature range 405° to 475°.

It was pointed out in the previous paper that pyrolysis of polymers, unlike molecular distillation, is a very slow process. While in the latter case only distillation is involved, in the case of pyrolysis, distillation follows fragmentation and the rate of the combined process is necessarily that of fragmentation. In view of this, the vapor phase will be very unsaturated, even with regard to the larger fragments at the high temperatures employed and will, therefore, not be very sensitive to the total pressure. On comparing the work of Staudinger and Steinhofer, who pyrolyzed polystyrene at a pressure of 0.1 mm. Hg, with that of Madorsky and Straus who used a pressure of about 10^{-5}, it was found that the results were about the same, the yield of the monomer being 43.5 per cent and 40 per cent of the total pyrolyzed part, respectively. A comparison of the yield of isoprene obtained in this investigation with those found in the literature, is given in Table XVI. The yields are shown in percent of total pyrolyzed part. There seems to be a good agreement between the yield obtained in the present work with that obtained by Staudinger and Fritschi, at a pressure of 0.1 to 0.3 mm., or even with that of Staudinger and Geiger at a pressure of one atmosphere, the values being 5.15, 4.9 and 4.2%, respectively. As to Wall's work, who worked

TABLE XVI. Yield of Isoprene in the Pyrolysis of Natural and Synthetic Polyisoprene. Comparative Results Obtained by Various Investigators

Investigators	Ref.	Polymer	Temp., °C.	Rate of heating	Pressure, mm.	Weight of sample, g.	Yield of isoprene, %
Present work	-	Synthetic polyisoprene	300-400	Slow	10^{-6}	0.050	5.15
Staudinger-Fritschi	4	Natural rubber	275-320	Slow	0.1 to 0.3	170	4.9
Staudinger-Geiger	5	Natural rubber	300-400*	Slow	760	100	4.2
Wall	9	Synthetic polyisoprene	400	Slow	10^{-3}	0.001	5
Wall	9	Balata	400	Slow	10^{-3}	0.001	2
Wall	9	Natural crepe	400	Slow	10^{-3}	0.001	2
Midgley-Henne	6	Natural crepe	700	Fast	760	7200	10
Bassett-Williams	7	Smoked crepe	580	Slow	760	250	8.3
Bassett-Williams	7	Smoked crepe	650	Fast	760	250	12.9
Bassett-Williams	7	Smoked crepe	600	Very fast	760	100	19.2

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*Temperature of pyrolysis is not given for this experiment. It was estimated to be in this range from the description.

at a temperature and pressure comparable to ours, but used samples of only 1 mg., there is good agreement with the present work in the case of synthetic polyisoprene, 5%, but not in the case of natural rubbers, where the yield was 2%. The yield obtained by Midgley and Henne, who worked at a temperature of 700° and at atmospheric pressure, was twice that obtained by Staudinger and co-workers or by us. Particularly interesting are the results of Bassett and Williams, who studied the effect of rate of heating on yield. The yield of isoprene was increased in their work from 8.3%, when the heating rate was slow to 12.9% when the heating was fast. On dropping 1 g. pieces of rubber on a hot metal surface, maintained at 600°, the yield of isoprene was raised to 19.2%.

Yields of the various fractions obtained in pyrolysis are summarized in Table XVII and the average molecular weights of these fractions are summarized in Table XVIII. Polystyrene is included in these tables for the purpose of comparison. Even in the case of polybutadiene and GR-S, where composition of fraction IIIA varies with temperature, the average molecular weight of the fraction as a whole is practically constant throughout the temperature range. In Table XVIII, the values for fractions II, IIIA and IV were determined experimentally, while those for fraction IIIB were estimated on the assumption that it consisted of a mixture of hydrocarbons with 8 to 15 carbons.

TABLE XVII. Summary of Pyrolytic Fractionation of Hydrocarbon Polymers (Average Values of Fractions)

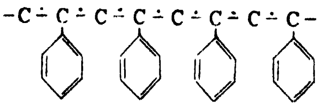
	Fractions in per cent of pyrolyzed part					
Polymer	II Waxlike	IIIB Liquid	IIIA Liquid	III IIIA+IIIB	IV CH_4	Yield of monomer
Polystyrene	57.8	-	-	42.1	0.10	40.00
Polyisobutene	68.3	9.5	22.	31.5	0.22	20.15
Polyisoprene	88.7	5.6	5.7	11.3	0.02	5.15
Polybutadiene	85.7	9.8	4.2	14.0	0.30	0.67.2.27
GR-S	88.0	7.9	3.9	11.8	0.19	1.71-2.14
Polyethylene	96.6	2.3	1.1	3.4	Trace	-

TABLE XVIII. Average Molecular Weights of Fractions Obtained in the Pyrolysis of Polymers

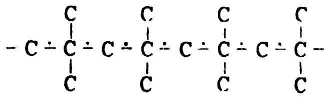
	Average molecular weights of fractions			
Polymer	II	IIIB	IIB	IV
Polystyrene	264	-	103.22*	16
Polyisobutene	543	150	57.12	16
Polyisoprene	577	150	68.45	16
Polybutadiene	739	150	51.00	16
GR-S	712	150	47.88	16
Polyethylene	692	150	53.06	16

*In the case of polystyrene, fraction III was not divided into IIIA and IIIB so that 103.22 is the average molecular weight of fraction III.

Fraction III contains the monomer as well as the other small fragments of pyrolysis. The yield of this fraction can be used as an indication of relative fragmentation of polymers during pyrolysis. In this respect, the polymers, as seen from Table XVII, fall into 3 groups: (a) polystyrene and polyisobutene, (b) polyisoprene, polybutadiene and GR-S, and (c) polyethylene. Fragmentation, or the relative number of scissions occurring in the chain during pyrolysis will be determined, on the one hand, by the frequency of low energy carbon-to-carbon bonds in the chain and, on the other hand, by the steric hindrance to the escape of fragments caused by side chains. Considering the structural formula of the various polymers studied, we find that in those of group (a) every carbon-to-carbon link has a lower energy than the ordinary link. Thus, in polystyrene every C-C link in the chain is in β position to a double bond:

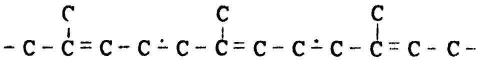


In this as in the structural formula below, dots indicate low-energy C-C links. Similarly, in the case of polyisobutene, every C-C link in the chain is weakened by the side chain attached to every other carbon in the chain:



$$-C\dot{-}\underset{C}{\overset{C}{C}}\dot{-}C\dot{-}\underset{C}{\overset{C}{C}}\dot{-}C\dot{-}\underset{C}{\overset{C}{C}}\dot{-}C\dot{-}\underset{C}{\overset{C}{C}}-$$

In the polymers of group (b) every fourth C-C link in the chain has a lower energy because of being in the β position from a double bond:



$$-C-\overset{C}{C}=C-C\dot{-}C-\overset{C}{C}=C-C\dot{-}C-\overset{C}{C}=C-C-$$

Polyisoprene

$$-C-C=C-C\dot{-}C-C=C-C\dot{-}C-C=C-C-$$

Polybutadiene

In the case of polyethylene, group (c), all the C-C links have the normal amount of energy.

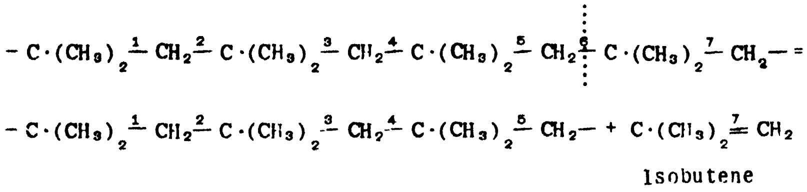
Relative thermal stability of polymers is illustrated in Figure 2, where percentage pyrolysis is plotted against temperature. Only those experiments which were of 30 minutes duration at the maximum temperature of the particular experiment, are plotted. The order of stability here is as follows:

polyethylene = polybutadiene > GR-S > polystyrene >

polyisobutene > polyisoprene

This order is in agreement with that found by Seymour (8).

On examining the mass spectrometer data for fraction IIIA obtained from polyisobutene, Table II, we find that, it consists, on the average, of 92.2 mole percent isobutene, 6.0% neopentane and 1.6% isobutene. The isobutene could form by splitting off from a free-radical end of a chain in this fashion:



$$-C\cdot(CH_3)_2\overset{1}{-}CH_2\overset{2}{-}C\cdot(CH_3)_2\overset{3}{-}CH_2\overset{4}{-}C\cdot(CH_3)_2\overset{5}{-}CH_2\overset{6}{\vdots}C\cdot(CH_3)_2\overset{7}{-}CH_2- =$$

$$-C\cdot(CH_3)_2\overset{1}{-}CH_2\overset{2}{-}C\cdot(CH_3)_2\overset{3}{-}CH_2\overset{4}{-}C\cdot(CH_3)_2\overset{5}{-}CH_2- + \underset{\text{Isobutene}}{C\cdot(CH_3)_2\overset{7}{=}CH_2}$$

Neopentane could be formed by first splitting off as a free radical at position 5 instead of 6 and then picking up hydrogen from the surrounding macromolecules. Isobutane could form from isobutene through saturation with hydrogen from the surrounding molecules.

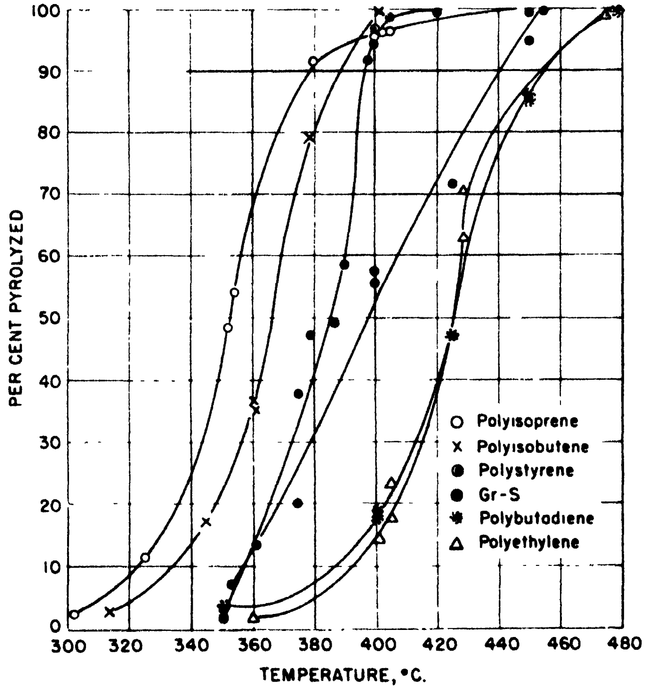


Fig. 2. Thermal decomposition of polymers.

In fraction III from polyisoprene, mass spectrometer analysis, Table V, shows it to consist of 90.8 mole per cent isoprene and 4.6 mole per cent pentenes, the rest being small amounts of mono or diolefins and cyclodienes. All of these could form by splitting off from a free radical end of a chain and transferring the free radical to the chain. For some reason no saturated compounds are found in this fraction.

Thermal decomposition of polyisobutene, polyisoprene and polystyrene, judging from the composition of their respective fractions

IIIA and III, follow simple patterns, consisting almost entirely of monomers, dimers, trimers, etc. In the case of polybutadiene, GR-S and polyethylene the decomposition patterns are rather complicated. In the decomposition of polybutadiene and GR-S, the yield of the monomer varies from about 60 to about 20 mole per cent of fraction IIIA, the other constituents being mostly straight chain paraffins, mono and diolefins and to a small extent, cyclodienes. The drop of monomer yield with rise in temperature, was observed only in the case of polybutadiene and GR-S. This drop may have been due to an increase in the content of the dimer, presumably, vinyl cyclohexene, at the expense of the monomer, with increase in temperature of pyrolysis. However, this should have been followed by a corresponding increase in fraction IIIB at the expense of IIIA. The work done on the separation of fraction III into IIIA and IIIB is insufficient to draw a definite conclusion in regard to the last point. The problem of monomer-dimer ratio in the case of pyrolysis of polybutadiene (also GR-S), is tied up with a similar problem of isoprene-dipentene ratio in the pyrolysis of polyisoprene and requires more work for its clarification.

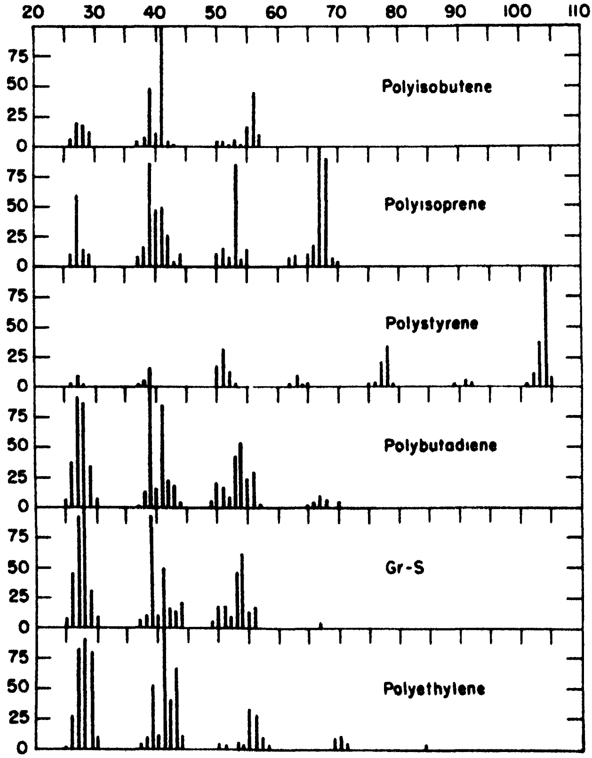


Fig. 3. Mass spectra of fractions III or IIIA. Abscissas are molecular weights, and ordinates are relative heights on a scale of 100 for the maximum peak.

In the pyrolysis of polyethylene very little of the small fragments is obtained. Fraction III appears to be constant throughout the temperature range studied. Judging from the composition of fraction IIIA, the fragments consist of straight chain paraffins and monoolefins and traces of diolefins. The most abundant constituents are butenes, followed by n-butane, n-propane and n-ethane.

Pyrolytic fractionation of polymeric substances, in conjunction with mass spectrometer analysis of the light fractions, offers an easy, quick and dependable method for the analysis of these substances. Each polymer gives a characteristic spectrum in the mass range up to about 105 as shown in Figure 3. With the further development of the mass spectrometer and the extension of its range to higher masses, this new method should prove valuable not only in the identification and determination of purity of polymers and copolymers, but in the study of their structure and properties as well. By connecting the pyrolysis apparatus directly to the mass spectrometer, analysis of the more volatile fractions could be further facilitated and expedited.

The authors express their indebtedness to F. L. Mohler for many helpful suggestions, to R. M. Reese who operated the mass spectrometer and to M. Tryon who purified most of the polymers used in this work.

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Synopsis

Samples of polyisobutene, polyisoprene, polybutadiene, GR-S, and polyethylene, weighing about 25 to 50 mg., were pyrolyzed in a vacuum of about 10^{-6} mm. of mercury in a specially designed apparatus at temperatures ranging between 300 to 475°C. The volatile products of pyrolysis were separated into four fractions: (IV) gaseous, volatile at -196°; (IIIA) liquid, at -75°, (IIIB) liquid, at 25°; and (II) waxlike fraction, volatile at the temperature of pyrolysis. The gaseous fraction was analyzed in the mass spectrometer and was found to consist in all cases of CH_4. The liquid fraction, IIIA, was analyzed similarly and was found to give a mass spectrum characteristic for any given polymer. A molecular weight determination of the waxlike fraction by the micro freezing point-lowering method, showed it to vary from 543 to 739, depending on the polymer from which the fraction was obtained. It is shown that the method of pyrolytic fractionation of high molecular weight polymers, in conjunction with mass spectrometer analysis of the more volatile fractions, can serve as a means of identifying the polymers.

Résumé

Des échantillons de polyisobutène, polyisoprène, polybutadiène, GR-S, et polyéthylène, pesant de 25 à 50 mgr., ont été soumis à pyrolyse sous vide (10^{-6} mm. de mercure), dans un appareil spécialement construit à cet effet, à des températures allant de 300° à 475°C. Les produits volatiles de la pyrolyse ont été séparés en quatre fractions: (IV) produits gazeux, volatile à -196°; (IIIA) produits liquides à -75°C.; (IIIB) produits liquides à 25°; et (II) fraction cireuse, volatile uniquement à la température de pyrolyse. La fraction gazeuse a été analysée au spectromètre de masse, et était constituée dans tous les cas de méthane. La fraction liquide, IIIA, a été analysée de la même façon, et fournit un spectre de masse caractéristique pour chaque polymère déterminé. Une détermination du poids moléculaires de la fraction cireuse par la méthode micro-cryoscopique, indique des valeurs de 543 à 739 suivant le polymère dont on est parti pour obtenir ce produit. Cette méthode de scission pyrolytique des hauts polymères, doublée d'une analyse au spectromètre de masse pour les fractions les plus volatiles, peut servir de moyen d'identification des polymères.

Zusammenfassung

Proben von Polyisobutylen, Polyisopren, Polybutadien, Buna-S und Polyaethylen, zwischen 25 und 50 mg. wiegend, wurden unter einem Vakuum von 10^{-6}mm. Quecksilber in einem besonders zu diesem Zwecke entworfenen Apparate bei Temperaturen von 300 bis 475°C. pyrolysiert. Die fluechtigen Pyrolyseprodukte wurden in vier Fraktionen geteilt: (IV) gasfoermig, fluechtig bei -196°C.; (IIIA) fluessig bei -75°C.; (IIIB) fluessig bei 25°C.; und (II) wachsfoermig, fluechtig bei der Pyrolysentemperatur. Die gasfoermige Fraktion wurde massenspektrometrisch analysiert und bestand in allen Faellen aus Methan. Die fluessige Fraktion IIIA wurde aehnlich analysiert und ergab ein Massenspektrum, das fuer ein gegebenes Polymerisat charakteristisch war. Eine Molekulargewichtsbestimmung der wachsfoermigen Fraktion durch die Mikroschmelzpunktniederungsmethode ergab Werte zwischen 543 und 739, je nach dem Polymerisat, von dem die Fraktion abstammte. Es wird gezeigt, dass die Methode der pyrolytischen Fraktionierung von Polymeren hoher Molekulargewichte mit Anwendung von massenspektometrischer Analyse der fluechtigeren Fraktionen zur Identifizierung von Polymerisaten dienen kann.

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LETTER TO THE EDITORS

INTRAMOLECULAR REACTIONS IN VINYL COPOLYMERS

Merz, Alfrey and Goldfinger (1) have extended Flory's (2) statistical treatment of the dechlorination of polyvinyl chloride by metallic zinc to the case of copolymers of vinyl chloride. They derive the following expression:

$$f = e^{-2P_{aa}} \tag{1}$$

where f represents the fraction of chlorine remaining in the copolymer, P_{aa} is the probability that a vinyl chloride free radical will react with a vinyl chloride molecule during the copolymerization. In a later section of their paper, they extend the equation to allow for the effect of the next-to-the-end group in the growing free radical. Their result is given by:

$$f = 1 - \frac{P_{baa}}{P_{aaa}} (1 - e^{-2P_{aaa}}) \tag{2}$$

Here, P_{baa} is the probability that a vinyl chloride free radical, formed by the addition of a vinyl chloride molecule to a free radical of the comonomer, will add another vinyl chloride molecule.

The sequence-length distribution function that applies in this case does not hold for sequences of unit length, as is pointed out by these authors. However, we find that they have not consistently corrected for this in the derivation of equation (2). A corrected derivation is given below.

The number fraction N_n of sequences of A monomer units of length n is given by:

$$N_n = P_{baa} P_{aaa}^{n-2} (1 - P_{aaa})$$

for n > 1, and by:

$$N_1 = 1 - P_{baa}$$

for n = 1.

The value of f, the fraction of unremoved substituents, then is given by:

$$f = \frac{S_1(1 - P_{baa}) + \sum_{n=2}^{\infty} S_n P_{baa} P_{aaa}^{n-2}(1 - P_{aaa})}{(1 - P_{baa}) + \sum_{n=2}^{\infty} n P_{baa} P_{aaa}^{n-2}(1 - P_{aaa})}$$

Evaluation of this expression leads to the result:

$$f = 1 - \frac{P_{baa}}{P_{aaa}(1 - P_{aaa} + P_{baa})}(1 - e^{-2P_{aaa}})$$

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REVIEW

Encyclopedia of Chemical Technology, Volume 2, Raymond E. Kirk and Donald F. Othmer, editors. Interscience, New York, 1948, xvi + 915 pp. 20.00 per volume.

In this second volume of "Encyclopedia of Chemical Technology," which is to appear in about ten volumes, the editors again present an excellent series of articles written by scientists in industrial laboratories and universities who are qualified by personal experience to write authoritatively about their subjects.

This volume contains articles on a wide variety of subjects ranging from discussions on Atomic Structure, Calorimetry and Calculations, through articles on a number of inorganic chemicals, metals and minerals, organic chemicals, dyes, and pharmaceuticals and miscellaneous industrial products.

Inorganic topics include the production, chemistry, economic aspects, and applications of the following elements and their alloys and/or compounds: Antimony, Arsenic, Barium, Beryllium, Bismuth, Boron, Bromine, Cadmium, and Calcium.

Topics of interest to organic chemists particularly include Benzene, Benzaldehyde, Benzene Sulfonic Acid, Benzidine, Benzoic Acid, Benzophenone, Benzoyl Peroxide, Benzyl Alcohol and β-Phenylethyl Alcohol, Betaines, Butadiene, Butyl Alcohols, Butyl Amines, Butyraldehyde, Butyric Acid and Butyric Anhydride, Caffeine, Camphor, Carbohydrates, Azine Dyes, Azo Dyes, Azoxy Compounds, and Azomethanes.

Those interested in biologically important materials and pharmaceuticals will find articles on Antibiotics, Barbituric Acid and Barbiturates, Blood Fractionation, Ascorbic Acid, Antiseptics, Disinfectants and Fungicides, Bile Constituents, Biotin, Antianemia Preparations, Antiscorbutics, Antispasmodics, and Astringents.

Miscellaneous industrial processes and products are discussed in articles on Antifreezes, Antioxidants, Asbestos, Asphalt, Bagasse, Bakery Processes, Baking Powder, Batteries, Bearing Metals, Beer and Brewing, Bituminous Roofing Materials, Animal Blood, Brake Linings, Building Materials, Calking, Candles, Active Carbon, Carbon Arc, and Carbides.

Articles which may be of direct interest to those who work with high polymers include those on Benzoyl Peroxide, Butadiene, Butyraldehyde and Butyric Anhydride, Camphor, Plasticizers, Dyes, Antibiotics, Blood Fractionation, Antioxidants and Asphalt, while polymer science may be of less obvious relevance to other subjects as well - we learn that Bakery Processes depend on the formation of gas-retaining films from the protein of wheat.

In general, the articles are well written and refer to both historical background and the recent literature. They are descriptive, and contain flowsheets, photographs, bibliographies, and summaries of pertinent quantitative physical, chemical, and technological data. The Encyclopedia may be highly recommended as a convenient source of information which will be very useful to chemists and engineers both in research and in development and production.

Saul G. Cohen

Journal of Polymer Science Vol. IV, pp. 669-670, 1949

REVIEW

"Surface Chemistry for Industrial Research." J. J. Bikerman. Academic Press, New York, ix + 414 pp. (illustrated), 8.00

The emergence and growth of surface and colloid science into established disciplines may now be recognized as among the important developments in chemistry during the first three decades of the twentieth century. The widespread appreciation of the great industrial value of these subjects has led quite naturally to the need for a book on applied surface chemistry. "Surface Chemistry for Industrial Research," written by an author well qualified for the effort in this new direction, may be regarded therefore as a timely response to the demand for a monograph written "for people who know what is being done in their plant but want to know why it is done in a certain way and whether it can be done better." As an exposition of the relevance of the fundamental principles governing surfaces to practical situations, however, the book seems best viewed as only partially successful.

The general features of "Surface Chemistry for Industrial Research" are to be recommended: the pattern of the treatment of the subject is comprehensive, and the text is amply documented by references drawn from the full range of the international literature. The author's evident familiarity with the modern Russian publications on applied colloid science is especially valuable. Technically, the book is well illustrated; the device of subsection numbering makes for easy cross-reference. The exposition is characterized by its clear, terse style, and by the inclusion of many critical observations which reveal much acute thought.

The discussion, when examined more closely, however, is found to be marred by the sometimes extreme unevenness in the relative emphasis given to the various aspects of the subject. This predominant feature seems to result in part from the author's stated intention that the book contain a minimum of theory. Those sections dealing with the measurement of surface tension may be used to exemplify this point. The convenient, accurate and industrially widely used ring, drop weight and pendant drop methods do not receive the kind of documented exposition essential for their use by the applied research worker. The excessive condensation of theory also results in an inadequate discussion of the celebrated Gibbs' adsorption theorem. This principle, because of its enormous importance in surface chemistry, would seem to merit a complete, modern, and rigorous exposition even in a book on applications of the science.

On the other hand, those sections of the book dealing with the experimental evidence for the roughness of solid surfaces are quite good, and should go far to correct the academic tendency to regard such interfaces as smooth. Likewise, Chapter V, which is devoted to a discussion of the phenomena at solid-liquid-gas and solid-liquid-liquid, has been found most interesting and valuable. Although the book probably will not prove satisfactory if used as text, it will almost certainly be of use to advanced research workers, pure and applied, as a reference monograph.

G. E. Boyd

Journal of Polymer Science Vol. IV, pp. 671-672, 1949

REVIEW

"Organic Chlorine Compounds." Ernest Hamilin Huntress. Wiley, New York, 1948, xxv + 1443 pp., 27.50.

It was by great good fortune that this excellent compendium came to hand in time for editing the manuscripts for the articles on organic chlorine compounds for the Encyclopedia of Chemical Technology, Volume 3. Dr. Huntress' handbook proved extremely useful for our purpose, and this review is based largely on the real workout we gave the book.

Although Dr. Huntress disclaims any characterization of his work as a specialized Beilstein, it does approach the German work in its much greater coverage than the earlier Huntress-Mulliken "Identification of Pure Organic Compounds." The new volume covers 1320, but not all organic chlorine compounds of "Order III" (compounds of carbon with chlorine, with chlorine and oxygen, with chlorine and hydrogen, and with chlorine, hydrogen, and oxygen). It gives abundant references, but not all references, even through 1945; only the more important references for 1946-1947 have been given in a "Memorandum" before the Introduction. The attention given comparable compounds sometimes varies surprisingly; thus methyl chloride is given slightly over one page, whereas ethyl chloride rates over ten pages. For vinyl chloride it is stated that no attempt was made to cover polymerization, polymers, or copolymers, whereas a few such references are given for vinylidene chloride.

Perhaps the classification by physical properties and the designation of each compound by an arbitrary "location number" meets the needs of analytical chemists, but we found it most annoying to have to look, for example, in four different parts of the book for the mono- and dichlorobenzenes. The headings for the pages (e.g., "Division B, Section 2" on the left page if the name of a compound is in bold-face capitals on the page, and "Liquids with $D_4^{20} < 1.15$") are of no help to the average reader, who is not going to make a study of the elaborate system. Of real help, of course, are the five indexes, all giving "location numbers" instead of page numbers: by empirical formulas (essentially the Richter system, not beloved by all American chemists); by empirical formulas by percentage chlorine content; by empirical formulas by molecular weights; by 8 chemical types; and alphabetically by name (including synonyms).

The use of many synonyms and of structural formulas are excellent features, since there is as yet no general agreement on preferred names. The names on the whole seem to be fairly well chosen and unambiguous; the use of the German "fore-and-aft" type of name (as "1-chloroheptyne-1") should not confuse anyone used to the "fore" names approved by the International Union of Chemistry and preferred by Chemical Abstracts. In some cases the selections are puzzling: Why "Chloromethane," "chloroethene," and "ethyl chloride"? The use of synonyms is really necessary in such cases. Position numbers are sometimes used when they are not needed, as in 1,1,2-trichloroethylene, but they do no harm.

Under each compound prominence is given in boldface to Beilstein references (where available for the longer-known compounds), melting points, and boiling points, even though considerable space is often wasted because they are given in columns. The only other physical constants given regularly are specific gravity and refractive index. The listing of many values for constants without attempt at a really critical selection is no doubt a wise change from the earlier volume on compounds of "Order I," but makes the selection of one value difficult for the nonexpert. Azeotropic mixtures seem to be covered thoroughly.

Much space is saved by the use of abbreviations and of C for the compound in question - the latter a somewhat irritating device, but perhaps justifiable. Subheadings in the longer sections greatly facilitate the location of material, but the overuse of brackets and parentheses and phrases like "see indic. refs." make for needless confusion. The attempted distinction between formation and preparation is not always clear cut, as the author points out. Extremely helpful are the notations about comprehensive reviews and important studies, and also the "negative entries" (statements about unreported reactions and compounds).

The references are given in the abbreviated form of Chemical Abstracts, and the inclusion of numerous patent references will please all those with any interest in technology. A commendable policy is the addition of references to Chemisches Zentralblatt and Chemical Abstracts where deemed helpful. But why use the abbreviation "Cent." for the old spelling "Centralblatt" instead of "Zent." or "C.Z." ? The apology for giving C. A. references for patents in addition to Zentralblatt references, or where the latter were not available, is quite understandable in view of the author's well-known partiality for the German abstract journal. The latter journal's abstracts of patents were indeed much fuller and better than C. A.'s for many years, but perhaps Dr. Huntress has not noticed the improvement in the C. A. patent abstracts in recent years.

An exceedingly careful job of proofreading must have been done because glaring errors seem to be rare. The most serious errors encountered in our use of Dr. Huntress' book were under 3-chloropropene-1 (allyl chloride): The products of the reaction with benzene in the presence of sulfuric acid and of ferric chloride are reversed (p. 950), and the melting point of N-allylsaccharin is given as 58° instead of 98° (p. 951).

Since the merits of this compilation far outweigh any disadvantages, it is highly recommended for purchase by all libraries and by all individual chemists interested in organic chlorine compounds. It should soon save the purchaser enough time to justify the outlay for it.

Janet D. Scott

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Water Content of Hydrophilic Phenol-Formaldehyde Resins: Vapor Pressure-Temperature Relationships

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I. INTRODUCTION

The large water content encountered during the preparation of the phenoplasts is due chiefly to the water originally present in the commercial grades of formaldehyde and phenol; however, a small amount is liberated by the chemical reaction. The phenol-formaldehyde ratio, the amount of catalyst, and the time of reflux are controlled so that the resin remains hydrophilic (1) when this type of resin is produced for casting. The excess water is removed by vacuum dehydration at a later stage of the process.

Condensation of the phenol and formaldehyde is slow in the absence of catalysts. Both acidic and basic materials may be used, the nature of the intermediate resin depending upon the choice of the catalyst. When an alkaline catalyst is used, the initial reaction products are phenol alcohols which are referred to as resols; these materials are soluble and fusible. Upon the application of heat, the condensation advances with a resulting increase in the molecular weight to form resites, insoluble and infusible products. After the formation of methylol phenols, the course of the resinification reaction is not clear. These resin intermediate products react so rapidly and form such a multitude of final products that it has been impossible to isolate and identify them.

Significance of the Water Content

Cast resins owe their exceptional machinability and other remarkable physical properties such as impact, flexural, and tensile strength to their original hydrophilic character and the subsequent separation of the minute water droplets during the heat hardening (1). Just as fillers in the older phenolic molding powders relieved internal stresses and strains, so the presence of water droplets in cast resins gives a more stable and balanced system. As the hydrophilic sol gradually changes to a hydrophobic gel, water is released and remains as dispersed droplets entrapped in the gel structure. The heat-hardened end-product still contains particles of water of colloidal size ranging from 0.2 to 0.8 microns. The amount of water and its degree of dispersion critically affect the appearance and physical properties of the cured resin (2).

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[1] Present address: Tennessee Eastman Corporation, Kingsport, Tennessee.

The economy factor also must be considered. The dispersed water droplets provide both opacity and improved physical properties without the aid of pigments and fillers and increase the yield of resin per given weight of the more expensive reactants.

Object of this Research

After reaction of the aqueous formaldehyde and phenol in the presence of dissolved sodium hydroxide as catalyst, the water content of the resin is about 51%. During dehydration, it is desired to reduce this water content to about 14%. The previous discussion indicates the necessity of careful control of the amount of water and its degree of dispersion to obtain the optimum physical characteristics for the cured resite.

A survey of available methods of water determination revealed a lack of reliable data and that these methods were too inconvenient and time consuming for a continuous process.

Existing physical methods (3) as the measurement of volume changes, refractive index and optical activity, specific gravity, absorption spectrum, viscosity, and electrical resistance were too dependent upon such factors as degree of polymerization, composition, and temperature and only indirectly related to the water content. Analytical methods as distillation and weighing and chemical analysis were too slow for following a continuous process. Therefore, it was desirable to develop a simple, rapid, relative method for the continuous determination of water content which could be used to follow the process of dehydration and to detect the end-point (the degree of dehydration producing the best dispersion of water in the resin). In order to standardize the values of a relative method, it was necessary also to develop an absolute method for the determination of water in the liquid resin.

Feith (4) presents an excellent literature survey of the significant methods for the determination of water content of phenolic resins under different conditions. He briefly discusses twelve physical and chemical methods used in various branches of industry for the determination of the water content of a variety of products and points out why these methods are not applicable to resols.

II. EXPERIMENTAL PROCEDURES AND APPARATUS

Preparation of the Resin

100 g. of commercial phenol were mixed with 200.0 g. of commercial 37% formaldehyde solution and 12.0 g. of a 25% solution of sodium hydroxide. The mixture was refluxed for 17 minutes, neutralized and acidified to a pH of 4.5 by the addition of approximately 19.5 g. of a 51% lactic acid solution. After acidification it was dehydrated at a pressure ranging from 50 to 30 millimeters of mercury and a temperature of 80°C. in order to remove the excess water and other volatile matter. The dehydration required from 1.7 to 2.5 hours, depending upon the vacuum available and the amount of volatile matter to be removed. Throughout the dehydration, frequent measurements were made to follow the process and to detect the exact end-point. Any modifications of this procedure are recorded in Section III.

Method of Measurement

The methods investigated for following the process of dehydration, detecting the end-point, and determining the absolute water content of the resol were: (a) electrical resistance measurements; (b) dielectric constant measurements; (c) vapor pressure-temperature measurements; (d) reaction of the water with calcium carbide; (e) solvent extraction of the water; (f) volatilization of the water; and, (g) Karl Fischer reaction.

Electrical resistance and dielectric constant measurements were unsatisfactory as continuous methods of following the dehydration process. Four methods for the absolute determination of water in a resol were investigated. The method using calcium carbide failed due to the necessity of reducing the viscosity of the resol, by the addition of some organic solvent, to enable chemical reaction to occur; the liberated acetylene gas was too soluble in the available solvents.

Vapor Pressure-Temperature Measurements

The apparatus illustrated in Figure 1 for the determination of vapor pressure-temperature relationships consisted of a one-liter, three-necked, round-bottomed flask in which were inserted a vacuum-sealed stirrer, thermometer, and a two-way vacuum attachment. Surrounding the flask was a constant temperature water bath.

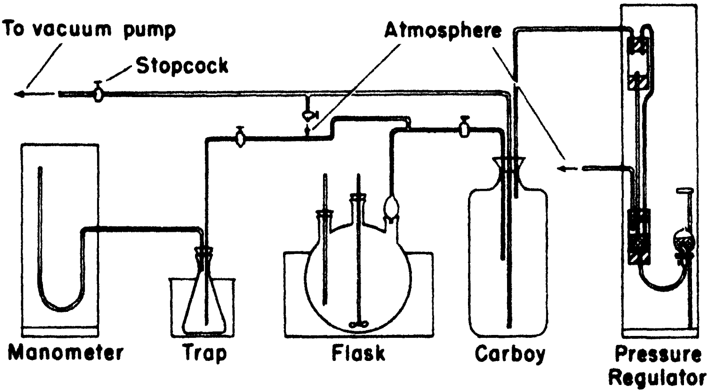

Fig. 1. Apparatus for vapor pressure-temperature measurements.

The stirrer maintained a uniform temperature throughout the resin. One outlet of the vacuum attachment passed through a condensation trap to a mercury manometer. The trap was surrounded by an ice bath and condensed any volatile vapors that might have contaminated the mercury of the manometer. The second outlet of the vacuum attachment passed into a five gallon carboy to which also was connected a water aspirator and an automatic, bleeder-type, pressure regulator. The aspirator was capable of reducing the pressure of the system to about 30 millimeters of mercury. The carboy was a buffer reservoir to minimize the effects of the bleeder-valve pulsations on the manometer fluctuations.

Whenever the pressure of the system became too low, the regulator bled air into the system to maintain any pressure for which it was set. Setting the regulator was a simple operation. When the pressure had increased sufficiently (as indicated by the mercury level of the manometer), the level of the mercury in the lower trap of the regulator was adjusted so that a seal was just made with the opening of the tapered tip of the right-hand tube. Thereupon, the stopcock of the mercury reservoir was closed, and the lower trap cut off suction of air through the right-hand tube of the regulator and into the system. If the pressure became too low, mercury rose in both tubes of the regulator to depress the level in the lower trap and open the right-hand tube to the atmosphere. Air entered the system through the right-hand tube until the pressure again increased sufficiently that the mercury level in the lower trap of the regulator was restored to its original position. The regulator maintained a constant pressure within about 4 millimeters of mercury.

Five glass stopcocks were inserted, as illustrated in Figure 1, to permit isolation of various parts of the system and to facilitate breaking the vacuum.

The apparatus was used to measure the dynamic vapor pressure at constant temperature. The resin solution was put into the previously described flask, and the temperature of the surrounding water bath was maintained between 80 and 85°C. The stirrer was adjusted to provide adequate agitation to ensure uniform temperature throughout the resin solution. The solution was dehydrated as rapidly as possible at as low a pressure as could be obtained with the water aspirator, 50 to 30 millimeters of mercury. At regular intervals, the system was opened to atmospheric pressure and the resin temperature permitted to rise to 80°C. During this time, a sample was removed for the determination of the absolute water content by another procedure. Then the automatic pressure regulator was connected into the system and the pressure was slowly decreased until the solution began to boil. Since at the boiling point of a solution its vapor pressure equals the external pressure, a manometer reading provided the vapor pressure of the resin at that stage of dehydration. By closing the appropriate stopcock, the pressure regulator again was cut out of the system and the dehydration was continued as rapidly as possible. Periodically, the procedure was repeated until dehydration was completed.

In order to calibrate the relative vapor pressure-temperature method, it was necessary to have some absolute method for the determination of water in the liquid resin. The solvent extraction, volatilization, and Karl Fischer methods were applicable.

Solvent Extraction Method

A Dean-Stark extraction trap type of apparatus was used. The distillation flask was immersed in an oil bath to obtain uniform distribution of temperature. To 30 g. of the resol, a mixture of 90.0 g. of cinnamyl alcohol and 30.0 g. of toluene was added. The solution was extracted from 3 to 9 hours until a constant reading was obtained. However, a qualitative analysis of the extract revealed not only water, but also formaldehyde and formic acid to be present. Therefore, it was necessary to analyze the extract to determine its true water content.

The extract was analyzed for per cent water by the Karl Fischer method, per cent formaldehyde by the hydroxylamine hydrochloride method (5), and per cent formic acid by an acid-base titration. The per cent total extract was checked on the original liquid resin by the volatilization method.

Volatilization Method

A small glass stirring rod and approximately 10.0 g. of sand were added to a 2-1/2 inch diameter pan. The pan and sand were dried 48 hours at 130°C. to expel all moisture and other volatile matter, cooled in a desiccator, and accurately weighed. From a glass weighing bottle, an accurately weighed sample of resol, between 0.5 and 1.0 g. was added to the sand. Approximately 3.0 milliliters of anhydrous methanol were added to thin the resol and permit more intimate mixture with the sand. The resol, sand, and methanol were mixed thoroughly with the aid of the stirring rod. The pan was returned to a convection-type oven and again baked at 130°C. until a constant weight was obtained in 72 to 120 hours. Then it was removed, cooled in a desiccator, and weighed. The per cent total volatile was calculated. For each sample, two determinations were made and their average value was recorded.

The per cent total water was calculated by multiplying the per cent total volatile by a factor obtained from the analysis of the distillate from the extraction method; the factor varied with the total volatile content of the resol and had to be determined for each stage of the dehydration.

A number of articles have been published on the application of oven dehydration, vacuum-oven dehydration and the effects of temperature upon the water content of resins (4,6), sugars (7), starches (8), wheat and flour (9), cereals (10), coal (10), proteins (10), and cellulose papers (10).

Karl Fischer Reaction

Two automatic reservoir burettes, fitted with dehydrite drying tubes, were placed so that their tips entered snugly fitting holes of a Bakelite jar cap; one burette contained Karl Fischer reagent and the other standard water-in-methanol solution. The Bakelite cap was also drilled to accommodate two platinum electrodes. The cap was of a size adapted to 250 milliliter Berzelius beakers; consequently, the beakers could be removed and replaced easily and quickly with minimum exposure to the moisture of the air. A magnetic stirrer provided agitation. The end-point of the titrations was detected with the aid of the commercial model Serfass Titration Unit which employed an electron ray or "electric eye" tube.

An accurately weighed sample of resol was transferred from a weighing bottle into a dry 250 milliliter Berzelius beaker. The weight of the sample was varied according to its approximate water content in order to provide a convenient titration. From a third automatic reservoir burette fitted with a drying tube, 40 milliliters of commercial, anhydrous methanol was added to the beaker. The anhydrous alcohol dissolved the resol and provided a liquid medium in which to immerse the platinum electrodes. The beaker then was placed into position in the previously described apparatus.

An excess of the reagent was added to the weighed sample; and then the excess was titrated with standard water-in-methanol solution until the free iodine color disappeared. The method is applicable to both liquids and solids containing as low as a few tenths per cent water. This procedure for per cent water was applied not only to the liquid resin but also to the distillate obtained in the extraction procedure.

There are several excellent references discussing the preparation and stability of the Karl Fischer reagent (11,12), the chemical reaction (11,12), a detailed decription of the apparatus (11,12) and the accuracy of the procedure (11). Applications of the Karl Fischer reaction to resols (4), resites (12), hydrated salts (13), cellulose products (14), and a general class of liquids and solids (11) are available.

III. EXPERIMENTAL DATA AND DISCUSSION

Vapor Pressure-Temperature Measurements

The composition of a homogeneoüs mixture of liquids is reflected by vapor pressure-temperature relationships. When the external pressure was held constant, the boiling temperature of the resol provided a reliable indication of the extent of dehydration. When the temperature was held constant, the vapor pressure of the resol indicated the extent of dehydration.

Several runs were made holding the external pressure constant and measuring the variations in boiling temperature throughout the dehydration. A very sharp increase in the slope of the temperature curve occurred at approximately the point of correct dehydration. Several runs also were made holding the temperature constant and measuring the variations in the vapor pressure of the resol as dehydration progressed. A very sharp decrease in the slope of the vapor pressure curve occurred at approximately the point of correct dehydration.

Although both methods appeared suitable to detect the point of correct dehydration, vapor pressure variations at constant temperature seemed the more satisfactory. During dehydration the vapor pressure at 80°C. changed about 350 millimeters of mercury; the boiling temperature at 40 millimeters of mercury changed only about 60°C. Consequently, as a control procedure, vapor pressure measurements would require less sensitive equipment and provide greater accuracy than temperature measurements.

The sharp decrease in the slope of the vapor pressure curve is easily explained. Originally the resol contains a large amount of "free" water which is readily liberated; at this stage the vapor pressure of the resol is essentially that of liquid water. As dehydration progresses, larger percentage of the remaining water is bound to the resin to form hydrous molecules. Energy is required to liberate this "bound" water. Consequently the vapor pressure of the resol decreases with decreasing water content, and the curve undergoes a sharp increase in slope when only the "bound" water remains. The end-point of dehydration falls along the steepest part of the vapor pressure curve where a slight decrease of water content causes a great decrease in vapor pressure.

To determine the point of correct dehydration, one merely maintains a constant temperature and measures the vapor pressure throughout the process by means of an automatic recording gage. When the existing vapor pressure agrees with the standard value for the specified temperature, the batch is properly dehydrated.

The vapor pressure of the resol at six separate temperatures was determined at various stages throughout the dehydration. The data are recorded in Table I and illustrated by Figure 2. Examination of Figure 2 reveals:

1. At corresponding temperatures, the vapor pressure of the resol was:
    a. higher than the vapor pressure of pure water at the start of dehydration.
    b. equal to that of water midway through the dehydration.
    c. far below that of water at the end of dehydration.

TABLE I. Vapor Pressure-Temperature Measurements (Catalyst, 9.0 g. of 25% NaOH Solution; Condensation Time, 20 minutes)

Total volatile, %	Temperature of resol, °C.	Vapor pressure of resol, mm. Hg.
53.4	70	275
	73	315
	76	352
	79	422
	82	442
	85	472
36.9	70	252
	73	282
	76	352
	79	405
	82	472
	85	482
30.9	70	217
	73	267
	76	307
	79	337
	82	372
	85	422
24.3	70	142
	73	162
	76	187
	79	222
	82	292
	85	322
17.4	70	122
	73	142
	76	172
	79	182
	82	190
	85	202
16.5	70	87
	73	82
	76	82
	79	82
	82	92
	85	82

2. The point of correct dehydration fell along the steepest part of the vapor pressure curve, making it very easy to detect the correct end-point by vapor pressure measurements.
3. The curves for different temperatures were rather evenly spaced at the start of dehydration and gradually converged to a point at a vapor pressure of 82-92 millimeters of mercury and a total volatile content of 16.5%. This seemed to substantiate the theory of a hydrous resin molecule and indicated 16.5% total volatile or 11.7% total water to be molecularly bound by the resin when 9.0 g. of sodium hydroxide solution were used as a catalyst. Probably, 82-92 millimeters of mercury represented the vapor pressure of the resol containing 11.7% molecularly bound water.
4. Apparently, the vapor pressure of the hydrous resin was not very sensitive to minor temperature differences.

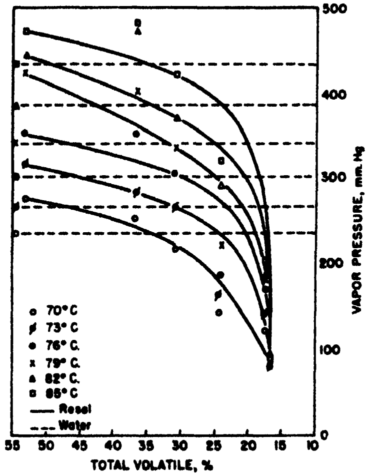

Fig. 2. Vapor pressure-temperature measurements (data of Table I).

Since the amount of "bound" water and the final vapor pressure of the hydrous resin depend somewhat upon the chain length of the polymer, the final vapor pressure should vary slightly with the amount of catalyst and the time of condensation. The data recorded in Table II and Figure 3 serve to illustrate the dependence of the final vapor pressure upon the degree of polymerization. The curves for 75°C. and 85°C. converged at a vapor pressure of 94 millimeters of mercury and a total volatile content of 14.9%. This indicated 14.9% total volatile or 10.6% total water to be molecularly bound by the resin when 12.0 g. of sodium hydroxide solution was used as a catalyst. A decrease in final water content of 1.1% was obtained by increasing the amount of catalyst (25% sodium hydroxide solution) 3.0 g. per 100 g. of phenol.

Slight variation of the final vapor pressure and water content with degree of polymerization does not lessen the value of vapor pressure-temperature measurements as a means of detecting the correct end-point of dehydration. Apparently, maximum stability of the cured resin depends primarily upon a minimum amount of "free" water in the resol at the casting stage, and not upon the total water content of the resol. Since the vapor pressure-temperature method bases the end-point of dehydration upon the vapor pressure of the hydrous resin rather than the total water content of the solution, minor variations in degree of polymerization are automatically compensated.

Several determinations were made to prove the reliability of vapor pressure-temperature control as a means of reproducing an exact end-point of dehydration. The data are recorded in Table III. Vapor pressure-temperature control of the dehydration of four separate samples resulted in a mean value of 18.6% total volatile, an average derivation from the mean of 0.25%, and a relative precision of 1.4%.

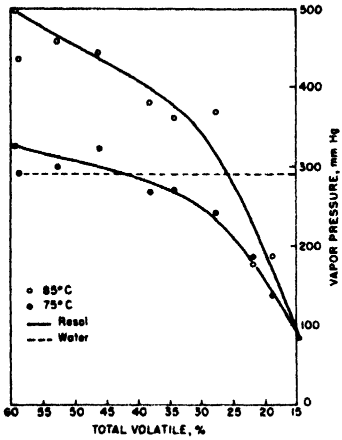

Fig. 3. Vapor pressure-temperature measurements (data of Table II).

TABLE II. Vapor Pressure-Temperature Measurements (Catalyst, 12.0 g. of NaOH solution; Condensation Time, 20 minutes)

Total volatile, %	Temperature of resol, °C.	Vapor pressure of resol, mm. Hg.
59.3	75	323
	85	496
52.7	75	297
	85	458
45.9	75	321
	85	441
38.0	75	267
	85	380
34.2	75	270
	85	361
27.7	75	241
	85	367
21.9	75	186
	85	176
18.7	75	119
	85	186
14.9	75	94
	85	94
14.9	75 85	Resin was about to gel; it stalled the stirring motor.

TABLE III. Vapor Pressure-Temperature Method

Sample No.	Wt. of resol before dehydration, g.	Dehydration				Volatile remaining after dehydration, %
		Wt. of volatile removed, g.	Resol temp., °C.	Resol vapor pressure, mm Hg.	Time of dehydration	
1	1000.0	459.9	80	80	2 hr., 15 min.	18.53
2	1000.0	455.9	80	80	1 hr., 45 min.	18.87
3	1000.0	464.7	80	80	2 hr., 20 min.	18.93
4	1000.0	463.6	80	80	1 hr., 50 min.	18.25

Solvent Extraction Method

Common methods of extraction (4) employing solvents such as xylene, toluene, and benzene were not applicable to resols; the resol polymerized to a solid state and entrapped part of the water.

To prevent solidification of the resin and enable all of the water to escape, a special blend of two solvents, cinnamyl alcohol and toluene, was used as the extraction medium. Since both solvents were immiscible with water, possible azeotrope formation presented no difficulty. As any azeotropic distillate cooled in the extraction trap, both solvents separated from the water layer and enabled the reading of the true water content.

Water, formaldehyde, and acid totaled about 95% of the extract. The remaining 5% might be accounted for by either analytical errors or the presence of small amounts of other components such as phenol, methanol, and the high boiling solvent.

The experimental data indicated the necessity of using the term total volatile rather than total water to express the results obtained by the extraction and volatilization methods. At the end of dehydration, the per cent total volatile as determined by either method was found to be approximately 71% total water; however, the actual water content of the total volatile varied and had to be determined at each stage of dehydration. Theoretically (15), the excess monoformaldehyde present in the resol polymerizes at the low temperatures of the initial stages of the vacuum dehydration process; the low vapor pressure of the polymerized formaldehyde causes the initial distillate to contain a high percentage of water. As dehydration progresses and "free" water is removed, the temperature increases sufficiently to decompose the polymerized formaldehyde to the monoformaldehyde; the high vapor pressure of the monoformaldehyde causes the final distillate to contain a lower percentage of water. Consequently, there is a gradual change in the water content of the total volatile matter present in the resol at successive stages of dehydration.

Volatilization Method

The volatilization method is applicable only to determinations where the time factor is of no consequence. Although this method cannot be applied to production processes, it was satisfactory for calibrating the vapor pressure-temperature method.

There was some doubt as to what temperature to specify for the volatilization method. By checking the composition of the volatile product and by correlating the per cent volatile as determined by the volatilization method, extraction method, and the Karl Fischer method, it appeared that 130°C. was the most suitable temperature for the volatilization method.

Karl Fischer Reaction

Feith (4) favors the Karl Fischer method above all others because the resol is entirely soluble in methanol at room temperature and no heat treatment is required. Several resols, analyzed by this method, showed comparable results in parallel tests. However, in all cases the values were much too low in comparison with other methods. This was attributed to the binding of part of the water by the resol molecules preventing its reaction with the iodine solution. By refluxing the resol with anhydrous methanol, Feith attempted to extract the presumably "bound" water and make it accessible for reaction with the Karl Fischer reagent. Refluxing the anhydrous methanol gave an increased water content compared with the cold method of analysis. This confirmed the hypothesis that part of the resol water was tightly bound. At the boiling point of methanol, 65°C., practically no "after condensation" of the resol took place and no water formation due to additional polymerization occurred.

Feith encouraged the belief that the Karl Fischer reagent determined only the "free" water in the resol and that to determine the "bound" water it was necessary to use an extraction procedure. The volatilization and extraction methods measured the total volatile ("free" water, "bound" water, and other volatile matter). A properly dehydrated resol was analyzed for total volatile and "free" water content. The results were:

Total Volatile:	
Extraction method with cinnamyl alcohol......	22.0%
Volatilization method at 130°C....................	21.7%
"Free" Water:	
Karl Fischer reagent................................	4.5%

It was desired to show the relationships of vapor pressure, "free" water, and "bound" water throughout the dehydration process. Vapor pressure was determined by the dynamic method; total volatile by the volatilization method at 130°C., total water by the extraction method and analysis of the extract; and "free" water by the Karl Fischer method. The summarized results are recorded in Table IV and illustrated in Figure 4.

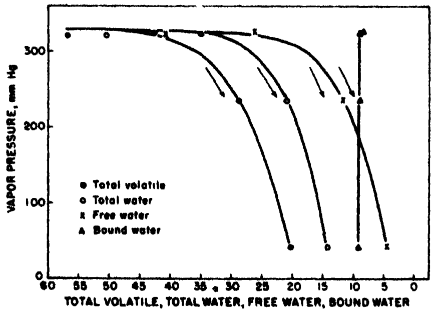

Fig. 4. Total volatile, total water, free water, bound water, and vapor pressure during hydration (data of Table IV).

That is, analysis of the resol, condensed 17 minutes and dehydrated to a vapor pressure of 43 mm. of Hg at 80°C., revealed:

Total volatile,%.....	20.1
Total water,%.......	14.3
Free water,%.........	4.9
Bound water,%........	9.4

Although not all of the "free" water was removed, it was reduced to a minimum.

TABLE IV. Total Volatile, Total Water, "Free" Water, "Bound" Water, and Vapor Pressure at Successive Stages of Dehydration

Sample No.	Vapor pressure at 80° C., mm.	Total volatile					
		Volatilization method, %	Extraction method, %	Water in extract, %	Total water, %*	Free water, %	Bound water, %
1	323	57.1	57.5	88.6	50.6	41.2	9.4
2	326	42.8	43.0	82.2	35.2	26.3	8.9
3	236	28.8	29.2	73.4	21.1	12.0	9.1
4	43	20.1	20.7	71.0	14.3	4.9	9.4

*Calculated from the per cent total volatile, as determined by the volatilization method, and the per cent water in the total volatile, as determined by a Karl Fischer titration of the distillate from the extraction method.

The very low vapor pressure of the resol at the end of dehydration might be attributed to the hydrous resin, and to the small amount of "free" water saturated with resin. Considering Raoult's law for the lowering of the vapor pressure of a volatile solvent by the addition of a nonvolatile solute, it is evident that the vapor pressure of the "free" water of containing such a high concentration of resin would be very low. Consequently, it would be impractical to remove all of the "free" water at the dehydration temperature employed.

Discussion of "Free" and "Bound" Water

The several experimental methods pursued in the investigation indicate the existence of both "free" and "bound" water in the hydrophilic resol at the casting stage. The "free" water was easily determined by a rapid Karl Fischer titration. The "bound" water had to be liberated by a dehydrating solvent or by an extraction procedure before it would react with the Karl Fischer reagent.

As previously mentioned, the condensation of formaldehyde and phenol in the presence of a basic catalyst produces a methylol phenol derivative. The $-\ddot{\underset{\cdot\cdot}{O}}-H$ radical is capable of holding two water molecules by hydrogen bonding. In addition, the $-\ddot{\underset{\cdot\cdot}{O}}-H$ radical also can hold an indefinite number of water molecules by electromagnetic attractions between the free electrons of the hydroxy oxygen atom and the hydrogen of the highly polarized water molecule.

The "bound" water accounts for the transparency of the hydrous resol. Further polymerization during the curing of the cast resin causes the enlarged molecules partially to lose their powers of hydrogen bonding and adsorption. Water of constitution also is liberated by the conversion of methylol groups to methylene linkages. Partial loss of the "bound" water accounts for the development of opacity; the less hydrous resite and the "free" water have widely different refractive indices. The rigid structure of the hydrophobic or fully polymerized resin encloses and retains the dispersed droplets of "free" water.

IV. SUMMARY

The significance of the water content to the physical properties of phenol-formaldehyde resins at various stages of preparation is briefly discussed. Available methods for the determination of water in such resins were found to be either unreliable or too elaborate for process control. We undertook to develop a simple, rapid, relative method for the continuous measurement of water content which can be used to follow the process of dehydration and to indicate the end-point which will result in the best dispersion of water in the cured resin. In order to standardize or calibrate such a relative method, it was necessary also to develop an absolute method for the analysis of water in the resol.

The composition of a homogeneous mixture of liquids is reflected by its vapor pressure-temperature relationships. During dehydration at 80°C., the vapor pressure of the resol decreases about 350 ml. of mercury. A very sharp increase in the slope of the vapor pressure curve occurs at approximately the proper degree of dehydration. At this stage a slight decrease in water content causes a very large decrease in vapor pressure. The sharp inflection in the curve is attributed to the existence of both "free" and "bound" water in the resin.

Vapor pressure measurements at a constant temperature have the following advantages: (a) Apparatus is inexpensive. (b) Operation is simple and rapid. (c) Measurements are practically independent of salt effects and small concentration variables. (d) Method is especially applicable to hydrophilic phenol-formaldehyde type resins. It depends primarily upon the "free" water content of the resol. (e) Large changes in the vapor pressure of the resol during dehydration make it very easy to detect the correct end-point.

Since the vapor pressure-temperature method bases the end-point of dehydration upon the vapor pressure of the hydrous resol rather than the total water content of the solution, minor variations in degree of polymerization are automatically compensated. Vapor pressure-temperature control of four separate batches of resin resulted in a mean value of 18.6% volatile, an average deviation from the mean of 0.25%, and a relative precision of 1.4%.

The solvent extraction method is applicable to the determination of total volatiles in the resin. It is necessary to use a special extraction mixture composed of cinnamyl alcohol and toluene to prevent solidification of the resol during reflux. Analyses of the extracts revealed the total volatile to contain water, formaldehyde, and formic acid. The volatilization method at 130°C. also is applicable to the determination of total volatiles in the resol and these analyses agree well with those obtained by the extraction method. The volatilization method was used to calibrate the vapor pressure-temperature method. The Karl Fischer method provides a means of measuring the "free" water in the resin.

Total water as determined by the extraction and volatilization methods minus "free" water as determined by the Karl Fischer reaction provides a measure of the amount of "bound" water held by the hydrous resol.

During the process of vacuum dehydration of the resin, while the "free" water decreases to approximately one-eight of its original content, the "bound" water remains substantially constant. The binding of water is attributed to the methylol groups of the resol molecules, and its release during the cure or hardening of the resin is considered to result from the conversion of these groups to methylene linkages.

Acknowledgment

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Synopsis

The significance of the water content to the physical properties of phenol-formaldehyde resins at various stages of preparation is

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During the process of vacuum dehydration of the resin, while the "free" water decreases to approximately one-eighth of its original content, the "bound" water remains substantially constant. The binding of water is attributed to the methylol groups of the resol molecules and its release during the cure or hardening of the resin is considered to result from the conversion of these groups to methylene linkages.

Résumé

L'influence de la teneur en eau sur les propriétés physiques des résines phenol-formaldéhyde, au cours des différents étages de la préparation, est brièvement discutée. Les méthodes disponibles pour le détermination de l'eau dans de telles résines sont, soit peu sûres, soit trop compliquées pour un procédé de controle. Le auteurs ont essayé de développer une méthode relative et simple, à la fois rapide, pour la mesure continuelle de la teneur en eau, afin de pouvoir suivre le procédé de déshydratation et d'indiquer le point final, qui correspondra à la meilleure dispersion de l'eau dans la résine préparée. En vue de standardiser et calibrer une telle méthode relative, il a d'abord fallu développer une méthode absolue pour l'analyse de l'eau dans un résol. La composition d'un mélange homogène de liquides est indiquée par ses courbes de tension de vapeur en fonction de la température. Durant la déshydratation à 80°C., la tension de vapeur du résol décroît d'environ 350 millimètres de mercure. Une augmentation très prononcée de la tangente de la courbe de tension de vapeurs se présente approximativement au degré de déshydratation adequat. À cette étage, une faible diminution dans la teneur en eau entraine une diminution très considérable de la tension de vapeur. L'inflection nette, que mainfeste la courbe, est attribuée à l'existence, à la fois, d'eau "libre" et d'eau "liée" au sein de la résine. Durant la déshydratation de la résine sous l'influence du vide, la teneur en eau "libre" diminue jusqu'approximativement le huitième de la teneur en eau initiale; la teneur en eau "liée" reste pratiquement constante. La liaison de l'eau est attribuée aux

groupes méthyloliques des molécules de résol, et sa diminution, au cours de la préparation ou du durcissement de la résine, est attribuée à la transformation de ces groupes en ponts méthyléniques.

Zusammenfassung

Die Bedeutung des Wassergehaltes in Bezug auf die physikalischen Eigenschaften von Phenolformaldehyd-Harzen in verschiedenen Stufen ihrer Bereitung wird kurz eroertert. Die existierenden Methoden fuer die Wassergehaltsbestimmung in solchen Harzen waren entweder unzuverlaessig oder zu schwierig fuer Kontrollzwecke. Es wurde versucht, eine einfache, schnelle, relative Methode zur ununterbrochenen Wassergehaltsbestimmung auszuarbeiten, mit deren Hilfe der Dehydrierungsprozess verfolgt werden kann und der Endpunkt, der der besten Zerstreuung des Wassers im gehaerteten Harze entspricht, gefunden werden koennte. Um eine derartige relative Methode zu standardisieren und kalibrieren, war es notwendig, eine absolute Methode fuer Wasseranalysen in diesen Harzen zu finden.

Die Zusammensetzung homogener Fluessigkeitsmischungen wirkt auf die Dampfdruck-Temperatur Beziehungen ein. Waehrend der Dehydrierung bei 80°C. nimmt der Dampfdruck eines Resolharzes um ungefaehr 350 mm. Quecksilber ab. Eine ploetzliche Vergroesserung in dem Abhang der Dampfdruckkurve findet ungefaehr bei dem richtigen Dehydrierungsgrade statt. Auf dieser Stufe verursacht eine kleine Verringerung des Wassergehaltes eine sehr grosse Verringerung des Dampfdruckes. Die scharfe Biegund in der Kurve wird dem Vorhandensein von sowohol "freiem" als such "gebundenem" Wasser zugeschrieben.

Waehrend der Vakuumdehydrierung des Harzes nimmt das "freie" Wasser bis zu einem Achtel des urspruenglichen Gehaltes ab, das "gebundene" Wasser bleibt unveraendert. Die Bindung des Wassers wird den Methylolgruppen der Resolmolekuelen zugeschrieben, und das Frei-werden waehrend der Harzverhaertung wird als eine Folge der Umwandlung dieser Gruppen zu Methylenquerverbindungen angesehen.

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Koresin and Related Resins[1]

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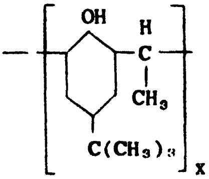
The German tackifier for butadiene-styrene type synthetic rubber called Koresin has been the subject of several communications during the last two years (1-6), and there is still some question concerning its structure. It is a condensation product of acetylene and p-tert-butylphenol prepared in the presence of zinc naphthenate and seems to be best represented by Formula I.



(I)

We had occasion to work on this tackifier during late 1944 and early 1945. A sample of the German product was furnished to us by Dr. R. F. Dunbrook, then Chief of the Copolymer Research Group of the Office of Rubber Reserve. It was at first thought that the product was an acid-catalyzed polymer from formaldehyde and p-tert-butylphenol. Then Dr. Miller Swaney of Esso Laboratories suggested to us that this resin might be made from acetaldehyde and tert-butylphenol in the presence of acid. This suggestion led us to study the formation of a series of resins from p-alkylphenols and aliphatic aldehydes. These resins were evaluated as tackifiers through the courtesy of Dr. J. N. Street by the research group at The Firestone Tire and Rubber Company.[3]

We also made extensive studies of the ultraviolet and infrared absorption spectra of Koresin and of the resins from aldehydes and phenols. There was a very close correspondence between these series, and we believe these data support Formula I for Koresin. The

[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] Allied Chemical and Dye Corporation Fellow, 1944-1945.

[3] We are indebted to Dr. O. D. Cole and Mr. L. A. Fickes (private communication through the Office of Rubber Reserve, April 25, 1945) for permission to include in this communication the tackifier ratings which they have determined for the polymers which we are reporting.

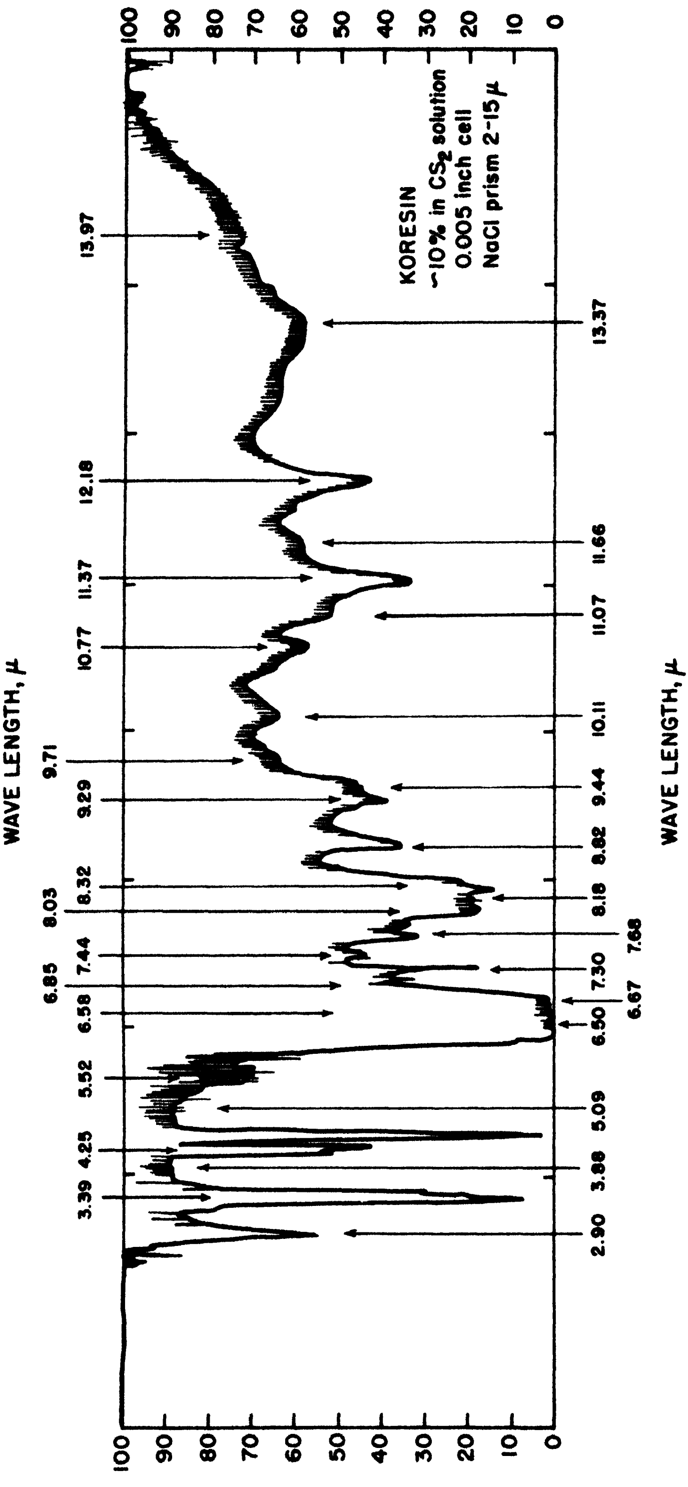

WAVE LENGTH, μ
13.97
12.18
11.37
10.77
9.71
9.29
8.32
8.03
7.44
6.85
6.58
5.52
4.25
3.39
KORESIN
~10% in CS_2 solution
0.005 inch cell
NaCl prism 2-15 μ
13.37
11.66
11.07
10.11
9.44
8.82
8.18
7.68
7.30
6.67
6.50
5.09
3.88
2.90
WAVE LENGTH, μ
100
90
80
70
60
50
40
30
20
10
0

Figure 1

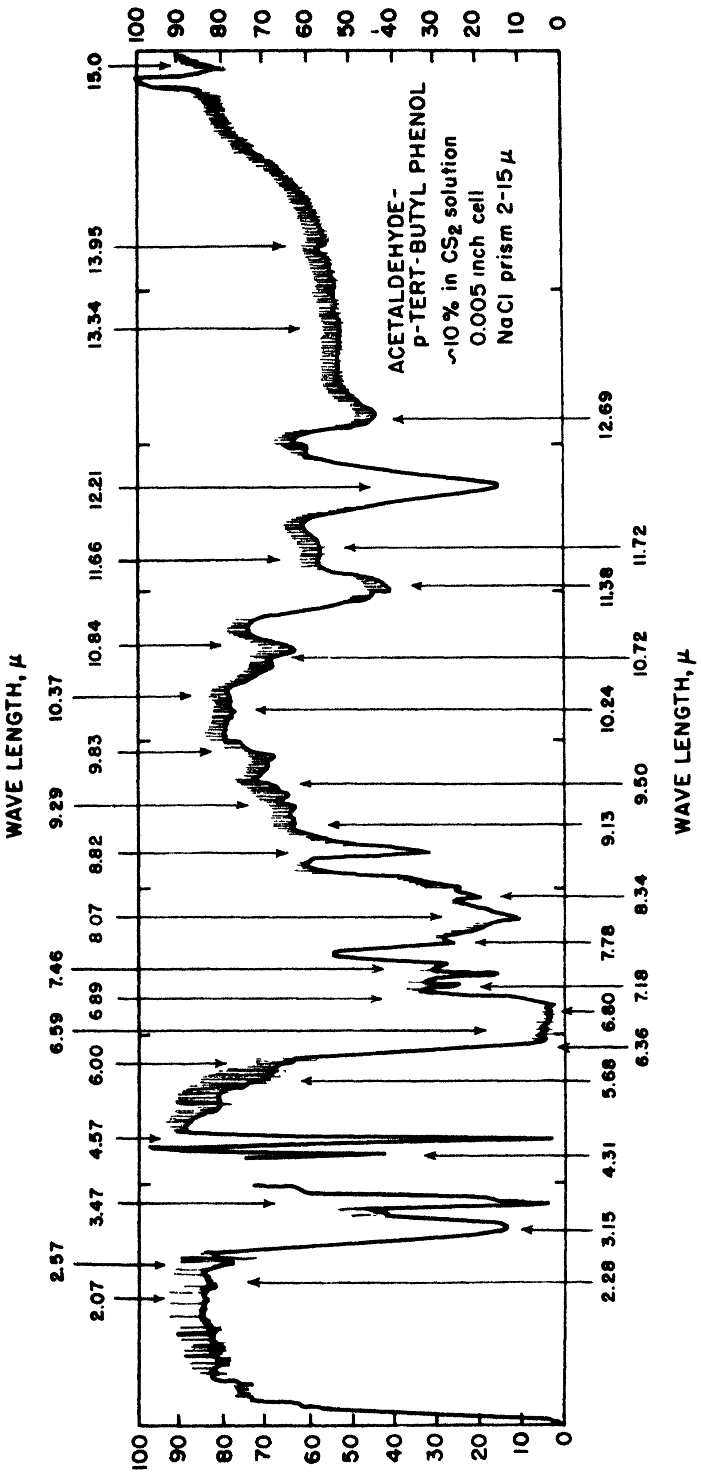

WAVE LENGTH, μ
2.07
2.57
3.47
4.57
6.00
6.59
6.89
7.46
8.07
8.82
9.29
9.83
10.37
10.84
11.66
12.21
13.34
13.95
15.0
2.28
3.15
4.31
5.68
6.36
6.80
7.18
7.78
8.34
9.13
9.50
10.24
10.72
11.38
11.72
12.69
WAVE LENGTH, μ
100
90
80
70
60
50
40
30
20
10
0
ACETALDEHYDE-
p-TERT-BUTYL PHENOL
~10% in CS2 solution
0.005 inch cell
NaCl prism 2-15 μ

Figure 2

principal difference between Koresin (Fig. 1) and the tert-butylphenol-acetaldehyde polymer (Fig. 2) was the presence in the infrared pattern of Koresin of some aliphatic double bond absorption (10.1 μ and 11.0μ). This would appear to mean that Koresin has a vinyl end-group, $-CH{=}CH_2$, which is not present in the acetaldehyde polymer.[4] A band which was tentatively assigned to an aryl group at 12.20μ is less pronounced in Koresin than in the acetaldehyde polymer, and the OH bands at 2.9μ in Koresin and at 3.0 μ in the acetaldehyde resin indicate a significant difference in hydrogen bonding in the latter polymer.

We were supplied with a sample of resin prepared from p-tert-butylphenol and acetylene in the presence of potassium hydroxide as a catalyst.[5] This material showed almost no activity as a tackifier (rating 1) although its molecular size (700-800 mol. wt.) was in the range usually effective. It is therefore interesting to note that its infrared absorption (Fig. 3) is very similar to that of Koresin except for the absence of the very strong hydroxyl band at 2.90μ which appears in the Koresin spectrum. These results suggest the importance of the hydroxyl groups in the tackifier activity of Koresin. Koresin also has bands of medium intensity at 8.15μ and 9.21μ and a weak band at 10.11μ which are not present in the alkali-catalyzed polymer. The polymer from crotonaldehyde and p-tert-butylphenol gives an infrared pattern (Fig. 4) similar to those of Koresin and the acetaldehyde polymer.

Ultraviolet absorption also indicated that Koresin and various tert-butylphenol-aliphatic aldehyde resins have very similar structures. Figure 5 compares the ultraviolet absorption of Koresin (curve 1) with those of a p-tert-butylphenol-formaldehyde resin (Arofene 775[6]) (curve 2), acetaldehyde resin (third entry in Table II) (curve 3), propionaldehyde resin (curve 4), and crotonaldehyde resin (curve 5).[7]

Since the resin prepared from acetaldehyde and p-tert-butylphenol showed some promise as a tackifier for GR-S (2), we prepared a number of other phenol-aldehyde polymers, and these are described in the experimental part. None of the phenol-aldehyde resins appeared to equal Koresin as a tackifier although in many cases they did show promise.

The phenol-aldehyde resins were in general prepared according to the directions given by Rust (7). The softening points of the resins were greatly influenced by the exact conditions of preparation. Under a given set of conditions with a given phenol the order of decreasing rate of resin formation for a series of aldehydes is: formaldehyde, acetaldehyde, crotonaldehyde, propionaldehyde. We found it desirable to use a higher ratio of volatile aldehyde than Rust suggests (7).

[4] We are indebted to Dr. J. R. Downing of the Chemical Department, Experimental Station, E. I. du Pont de Nemours and Company for the infrared curves reported here.

[5] We are indebted to Petroleum Chemicals, Inc., Baltimore, Maryland, for this material.

[6] We are indebted to Dr. Harry L. Fisher of U. S. Industrial Chemicals, Inc., for making this material available for our study.

[7] The ultraviolet absorption data were supplied by Drs. H. A. Laitinen and T. D. Parks.

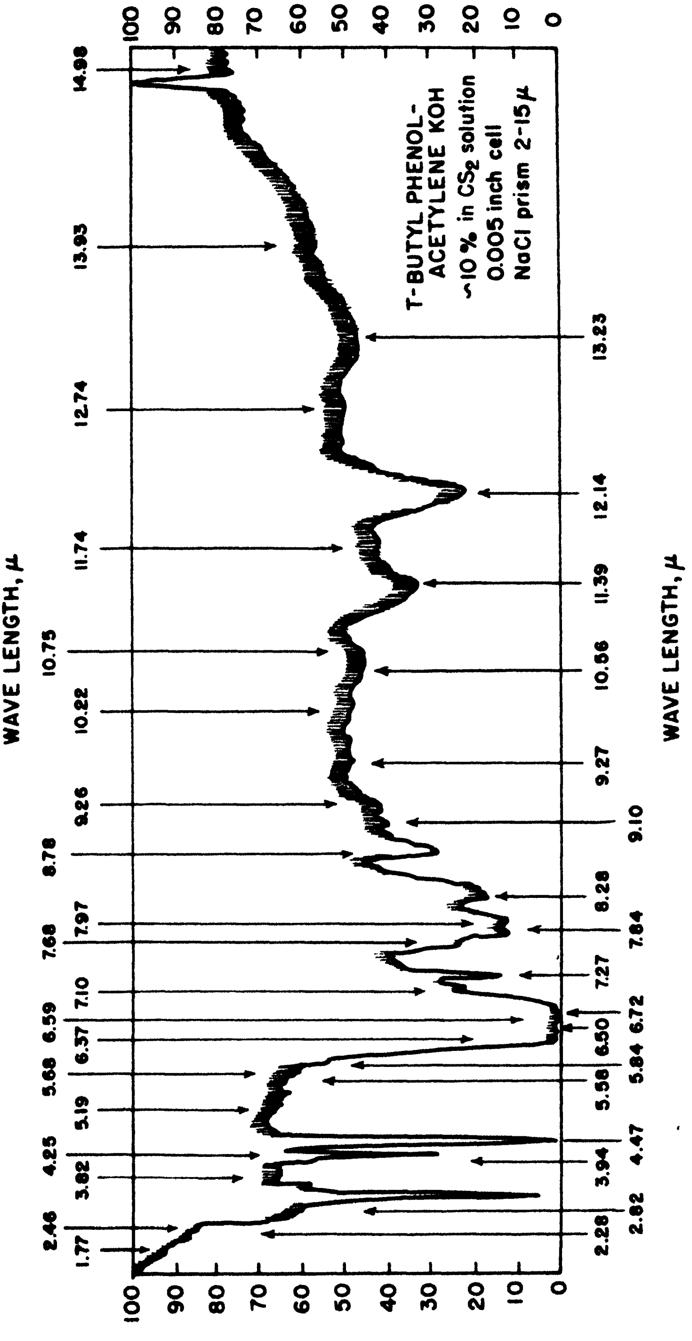

WAVE LENGTH, μ
1.77
2.46
3.82
4.25
5.19
5.68
6.57
6.59
7.10
7.68
7.97
8.78
9.26
10.22
10.75
11.74
12.74
13.93
14.98
2.28
2.82
3.94
4.47
5.58
5.84
6.50
6.72
7.27
7.84
8.28
9.10
9.27
10.56
11.39
12.14
13.23
WAVE LENGTH, μ
100
90
80
70
60
50
40
30
20
10
0
T-BUTYL PHENOL-
ACETYLENE KOH
~10 % in CS_2 solution
0.005 inch cell
NaCl prism 2-15 μ

Figure 3

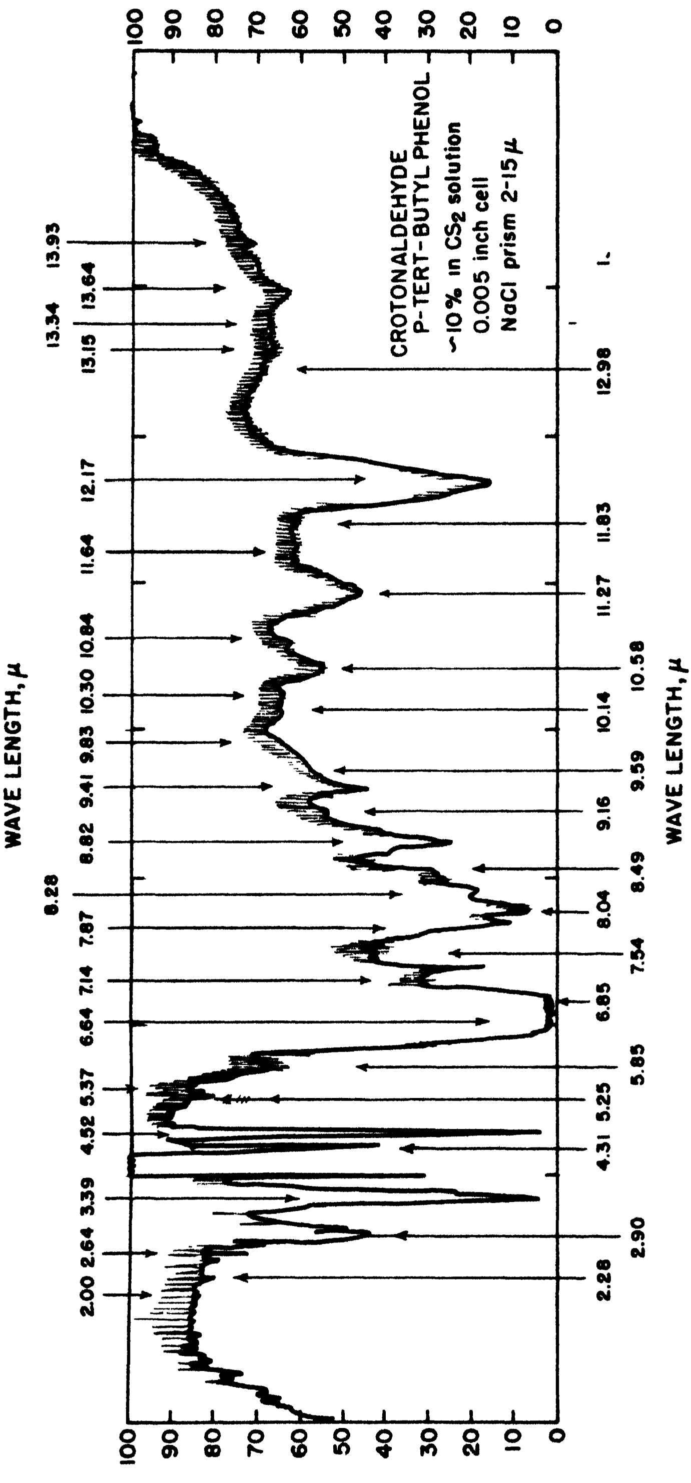

WAVE LENGTH, μ
2.00
2.64
3.39
4.52
5.37
6.64
7.14
7.87
8.28
8.82
9.41
9.83
10.30
10.84
11.64
12.17
13.15
13.34
13.64
13.93
CROTONALDEHYDE
P-TERT-BUTYL PHENOL
~10% in CS_2 solution
0.005 inch cell
NaCl prism 2-15 μ
2.28
2.90
4.31
5.25
5.85
6.85
7.54
8.04
8.49
9.16
9.59
10.14
10.58
11.27
11.83
12.98
WAVE LENGTH, μ
100
90
80
70
60
50
40
30
20
10
0

Figure 4

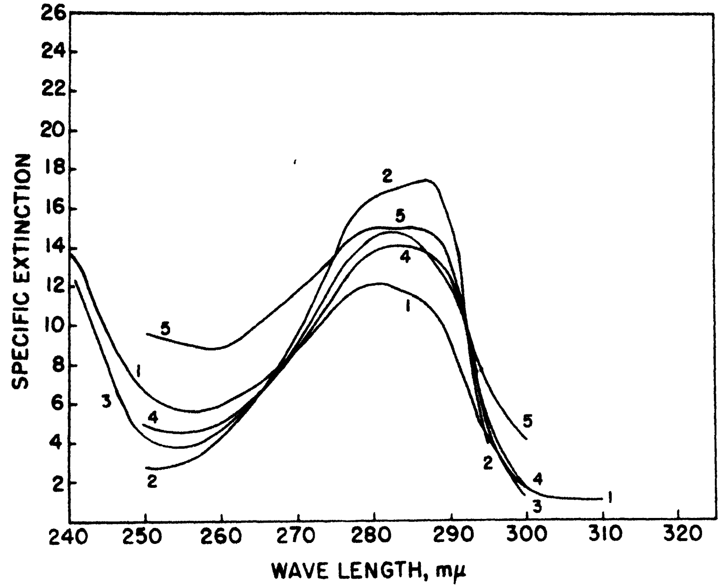


Figure 5

In one series of experiments with p-tert-butylphenol, acetaldehyde was replaced by ethylidene diacetate in the reaction mixture. The resin thus produced softened at 155-160° and had a molecular weight of about 1900-2000 where the acetaldehyde polymer softened at 120-125° and had a molecular weight of 900-1000.

EXPERIMENTAL

Preparation of Phenol-Aldehyde Resins

The procedure used in making the resins was essentially that of Rust (7). The following typical directions are those followed in making a p-tert-butylphenol-acetaldehyde resin with a softening point of 90-95°.

TABLE I. Effect of Water on the Resinification of p-tert-Butylphenol and Acetaldehyde

Phenol, moles	Aldehyde, moles	Water, moles	Temp., °C.	Reaction time, hr.	Softening point, °C.
1.5	6	8.3	140-150	44	75-78
0.5	1	2.8	110-120	20	90-95
1.5	2	2.8	130	4	110-115
0.5	0.66	0	140	0.75	119-123

A 500-cc. three-necked flask with standard taper connections was fitted with a 36-inch Allihn condenser and a glass, motor-driven stirrer. In it were placed 75 g. (0.5 mole) of p-tert-butylphenol, 30 g. (0.67 mole as acetaldehyde) of paraldehyde, 50 cc. of water, 5 g. of oxalic acid, and 15 cc. of concentrated hydrochloric acid. The mixture

TABLE II. Preparation of Phenol-Aldehyde Resins

Type of resin	Phenol, moles	Aldehyde, moles	Water, cc.	Oxalic acid, g.	Conc. HCl., cc.	Temp., °C.	Time, hr.	Softening point, °C.^{a}	Yield, %^{b}	Tackifier rating^3
p-tert-Butylphenol-acetaldehyde	1.5	6	150	15	45	145-150	44	75-78	89	4
	0.5	1	50	5	15	110-120	20	90-95	93	8
	1.5	2	50	15	45	130	4	110-115	92	9
	0.5	0.66	0	5	15	140	0.75	119-123	91	9
p-tert-Butylphenol-propionaldehyde	0.5	0.60	0	5	15	140-150	42	65-70	92	4
p-tert-Butylphenol-crotonaldehyde	0.5	0.56	0	5	15	150-160	2	80-85	91	10
p-Cresol-formaldehyde	0.60	0.66	--	(c)	(c)	110-120	21	90-95	89	0
p-Cresol-acetaldehyde	0.50	1	50	5	15	110-120	19	85-87	86	0
p-Cresol-propionaldehyde	0.50	0.80	0	5	15	145-150	20	70-75	92	2
p-Cresol-crotonaldehyde	0.50	0.56	50	5	15	120	18	75-80	84	1
	0.50	0.56	0	5	15	150-160	5	100-105	92	3
m-Cresol-formaldehyde	0.60	0.66	--	(c)	(c)	120	0.5	(d)	--	-
m-Cresol-acetaldehyde	0.50	1.3	50	5	15	125	15	108-112	72	0
m-Cresol-crotonaldehyde	0.50	0.56	0	5	15	140	0.10	(e)	--	-
m-Cresol-propionaldehyde	0.50	0.60	0	5	15	125	6	75-78	77	1
o-Cresol-acetaldehyde	0.50	1	50	5	15	130	18	108-113	81	0
	0.50	0.66	0	5	15	120	0.25	120-125	82	0
o-Cresol-propionaldehyde	0.50	0.60	0	5	15	145-160	17	80-85	90	0
o-Cresol-crotonaldehyde	0.50	0.56	0	5	15	140	0.5	120-125	81	-

Type of resin	Phenol, moles	Aldehyde, moles	Water, cc.	Oxalic acid, g.	Conc. HCl, cc.	Temp., °C.	Time, hr.	Softening point, °C.[a]	Yield %[b]	Tackifier rating[3]
p-Octylphenol-formaldehyde[f]	0.36	0.80	50	5	15	120	17	103-108	95	7
p-Octylphenol-acetaldehyde	0.36	0.66	0	5	15	150	2	80-85	92	8
p-Octylphenol-crotonaldehyde	0.36	0.56	0	5	15	150	3.5	55-60	102	10
	0.36	0.56	0	5	15	150	4	68-72	96	10
Tetrahydronaphthylphenol-acetaldehyde[g]	0.11	1.3	50	1	5	135	20	58-62	71	--
p-Cyclohexylphenol-crotonaldehyde	0.48	0.56	--	5	15	140	15	85-90	86	8
p-Cyclohexylphenol-acetaldehyde	0.48	0.68	--	5	15	130	4	125-130	86	--
o-Cyclohexylphenol-acetaldehyde	0.48	0.68	--	5	15	120	0.6	100-105	78	--
o-Cyclohexylphenol-crotonaldehyde	0.48	0.56	--	5	15	145	1.5	80-83	85	2
p-tert-Amylphenol-acetaldehyde	0.5	0.91	--	5	12	130	1	100-103	82	10
p-tert-Amylphenol-crotonaldehyde	0.5	0.56	--	5	15	140	4	65-70	82	10

Table continued on following page

TABLE II (concluded)

p-tert-Butylphenol-acetaldehyde, 9% zinc naphthenate [h]	0.5	0.67	--	5	15	130	0.5	110-115	84	8
p-tert-Butylphenol-crotonaldehyde, 9% zinc naphthenate [h]	0.5	0.67	--	5	15	150	2	74-78	94	8

---

[a] Softening points were taken in capillary tubes.

[b] Yields were calculated without consideration of oxalic acid which may have been present in the resin.

[c] Zinc chloride (1 g.) and phosphoric acid (1.5 cc.) were the catalysts instead of oxalic and hydrochloric acids.

[d] Resin did not soften when heated to 220°. It was separated by solution in absolute alcohol into a soluble fraction and an insoluble gel fraction. The soluble fraction was precipitated with water; it weighed 17 g. and softened above 200°.

[e] Resin worked up as in Note (d). Soluble fraction (30 g.) softened above 200°.

[f] p-tert-Octylphenol or 1-(p-hydroxyphenyl)-1,1,3,3-tetramethylbutane was supplied by the Resinous Products and Chemicals Company, Philadelphia, Pennsylvania.

[g] The tetrahydronaphthylphenol was supplied by the Chemical Department, Experimental Station, E. I. du Pont de Nemours and Company.

[h] Zinc naphthenate (7 g. per 0.5 mole of p-tert-butylphenol) was mixed with the resin during the period when it was heated to 220°. The zinc naphthenate was manufactured by Advanced Solvents using naphthenic acids supplied by Standard Oil of California.

was immersed in an oil bath, heated to 120°, and stirred at this temperature for twenty hours. After the reaction had run for several hours, 15 g. additional paraldehyde was added. The resin was washed several times with boiling water. It was then partially dehydrated by heating to 150° under a pressure of 50-100 mm. (water pump). The water pump was disconnected, and at atmospheric pressure the temperature of the bath was raised to 220-230° gradually during the course of about one-half hour. At this temperature the resin was very fluid and could easily be poured out on a copper plate where it solidified.

TABLE III. Analytical Data on Typical Resins

	Theoretical	Analysis, %[a]			
	empirical	Carbon		Hydrogen	
Type of resin	formula	Calcd.	Found	Calcd.	Found
p-tert-Butylphenol-acetaldehyde	$(C_{12}H_{16}O)_x$	81.79	81.32	9.15	9.09
p-tert-Butylphenol-propionaldehyde	$(C_{13}H_{18}O)_x$	82.04	80.25	9.53	9.17
p-tert-Butylphenol-crotonaldehyde	$(C_{14}H_{18}O)_x$	83.11	82.70	8.97	8.79
p-Cresol-formaldehyde	$(C_8H_8O)_x$	80.00	77.39[b]	6.71	6.55[b]
p-Cresol-acetaldehyde	$(C_9H_{10}O)_x$	80.55	79.48	7.51	7.60
p-Cresol-crotonaldehyde (S.P. 100-105°)	$(C_{11}H_{12}O)_x$	82.47	81.86	7.55	7.41
m-Cresol-acetaldehyde	$(C_9H_{10}O)_x$	80.55	79.10	7.51	7.14
o-Cresol-acetaldehyde	$(C_9H_{10}O)_x$	80.55	79.86	7.51	7.38
p-Octylphenol-formaldehyde	$(C_{15}H_{22}O)_x$	82.52	81.36	10.16	10.25

[a] The microanalyses reported in this manuscript were by Howard Clark of the Illinois State Geological Survey.

[b] Ash approximately 1.2%

The rate of reaction and the softening point of the resin were greatly dependent upon the amount of water used in the reaction mixture. Decreasing the water concentration reduced the time necessary for resinification and raised the softening point of the resin. These effects are illustrated in Table I.

In some experiments in which formaldehyde was condensed with an alkylphenol the catalyst was a mixture of zinc chloride and 85% phosphoric acid instead of oxalic and hydrochloric acids. Many of the resins were made without adding water to the reaction mixture other than that contained in the concentrated hydrochloric acid catalyst. Frequently, dehydration of the resin under vacuum was omitted. If resinification had proceeded until the product was very thick, it was simply washed, the washings decanted, the resin heated to 220° and poured. Table II includes experimental details for each resin prepared. The analyses of typical series are in Table III and the molecular weights in Table IV.

TABLE IV. Molecular Weights and Tackifier Action of Typical Resins

Type of resin	Softening point, °C.	Molecular weight[a]	Tackifier rating[3]
Koresin	130-135	1046; 1297	10
	122-140	----	10
p-tert-Butylphenol-formaldehyde[6] (Arofene 775)	115-120	773; 755; 752	9
p-tert-Butylphenol-acetaldehyde	75-78	469; 460	4
	90-95	494; 540	8
	110-115	778; 778	9
	119-123	844; 866	9
p-tert-Butylphenol-crotonaldehyde	80-85	444; 458	10
p-Cresol-crotonaldehyde	75-80	429; 412	1
	100-105	555; 584	3
o-Cresol-acetaldehyde	108-113	769; 853	0
	120-125	1250; 1332	0
p-Octylphenol-formaldehyde	103-108	1384; 1406	7
p-Octylphenol-acetaldehyde	80-85	824; 783	8

[a] By the Rast method. Dr. R. J. Dearborn did much of the experimental work on molecular weights.

p-tert-Butylphenol-Ethylidene Diacetate Resin

In a 500-cc., three-necked, round-bottom flask were placed 50 g. (0.33 mole) of p-tert-butylphenol, 50 g. (0.34 mole) of ethylidene diacetate, and 5 cc. of concentrated hydrochloric acid. The mixture was placed in a bath heated to 140° for a few minutes and then stirred at room temperature for twelve hours, and then again at 140° for twelve hours. During the course of one and one-half hours the temperature of the bath was raised to 230°. The mixture was then poured on a copper plate and allowed to harden. A light-colored resin which softened at 155-160° was the product. Ebullioscopic molecular weights in benzene solution were 1965 to 1995. This resin had a tackifier rating of 9.[3]

Ultraviolet Absorption Spectra[7]

The ultraviolet spectra were measured with a Beckman quartz spectrophotometer. Chloroform was the solvent in all cases and the concentrations employed varied from 30 to 60 mg./liter. Resin samples were dried in vacuo over phosphorus pentoxide before ultraviolet absorption was determined. The results are given in Table V.

TABLE V. Ultraviolet Absorption Spectra of Synthetic Resins

Resins	Softening point, °C.	Absorption peak, mμ	Specific extinction
Koresin	130-135	280	12.15
p-tert-Butylphenol-formaldehyde	115-120	287	17.40
p-tert-Butylphenol-acetaldehyde	90-95	286	14.95
p-tert-Butylphenol-propionaldehyde	65-70	284	14.18
p-tert-Butylphenol-crotonaldehyde	80-85	280	14.90
p-Cresol-formaldehyde	90-95	288	26.00
p-Cresol-acetaldehyde	85-87	284	18.47
p-Cresol-propionaldehyde	70-75	284	18.25
p-Cresol-crotonaldehyde	75-80	282	20.20
o-Cresol-acetaldehyde	108-113	280	16.38
m-Cresol-acetaldehyde	108-112	282	18.65
p-tert-Octylphenol-formaldehyde	103-108	288	10.78
p-tert-Octylphenol-acetaldehyde	80-85	282	11.62
p-tert-Octylphenol-crotonaldehyde	55-60	280	13.00

Infrared Absorption Spectra[4]

The records are direct recordings of per cent transmittancy of infrared radiation vs. wave length. The wave length assignments written on the records may not be accurate to 0.1 μ in some cases but comparison by matching records was precise to 0.01 μ. The resins were examined as 10% solutions in carbon disulfide.

Tackifier Ratings[3]

The ratings of some of the new polymers as tackifiers are listed in Tables II and IV. The tackifier ratings were determined in accordance with the general method of Smith, Ambelang, and Gottschalk (2). The values reported are on samples of GR-S (200 g.) which have been milled with 10% of their weight (20 g.) of the resin to be tested as a tackifier on a cool 12-inch laboratory mill, and after mixing well the mill was heated to 180-200°F. for a final one to two minutes of milling. The ratings are based on an arbitrary scale in which the tackiness of GR-S is set at 0 and that of a 10% mixture of Koresin in GR-S as 10.

The ratings given in Tables II and IV confirm the earlier reports (2) which show that the molecular weight of the resin bears some relation to its tackifier activity and that p-alkylphenols yield resins which have better tackifier action than those from the corresponding o-alkylphenols.

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Synopsis

The infrared and ultraviolet absorption spectra of Koresin are very similar to those of an acid-catalyzed p-tert-butylphenol-acetaldehyde polymer. This is believed to be evidence that Koresin has Structure I. A variety of phenol-aldehyde resins have been prepared for comparison with Koresin. The ratings of some of these materials as tackifiers have been reported. These furnish further evidence that the molecular weight of a phenol-aldehyde resin is important in its tackifying action. An alkaline-catalyzed condensation product of acetylene and p-tert-butylphenol shows no tackifying action and has no free hydroxyl in the polymer as judged by its infrared pattern.

Résumé

Le spectre infra-rouge et le spectre d'absorption ultraviolette du Korésine sont très semblables a ceux que l'on obtient au départ d'un polymère p-tert-butylphenol et acétaldéhyde (condensation en milieu acide). Ceci permet d'attribuer au Korésine la structure I. Différentes résines à base de phénol et d'aldéhyde ont été preparés pour comparer avec le Korésine. La valeur de certaines de ces substances comme "Tackifier" ont été indiquées. Ceci fournet une nouvelle preuve que le poids moléculaire d'une résine phenol-aldéhyde joue de rôle important dans le pouvoir "tackifying." Un produit de condensation, au milieur alcalin, de l'acetylène et du p-tertiaire-butylphenol ne manifeste pas de pouvoir "tackifying" et ne possède pas de groupes hydroxyles libres dans le polymère, comme il semble résulter des spectres infra-rouges.

Zusammenfassung

Die infraroten und ultravioletten Absorptionsspektren von Koresin sind denen eines durch Saeure katalysierten p-Tert-Butylphenol-Azetaldehyd Polymerisates sehr aehnlich. Dies deutet darauf hin, dass Koresin die Struktur I hat. Eine Anzahl von Phenol-Aldehyd Harzen wurde hergestellt, um sie mit Koresin zu vergleichen. Einige dieser Substanzen wurden als Klebrigkeits-Verursacher bewertet. Die Ergebnisse weisen darauf hin, dass das Molekulargewicht eines Phenolaldehydharzes in seiner Wirkung als Klebrigkeitsverursacher von Bedeutung ist. Ein alkalisch katalysiertes Kondensationsprodukt von Azetylen und p-Tert-Butylphenol ist kein Klebrigkeitsverursacher und enthaelt, mit Hinblick auf das infrarote Spektrum, keine freien Hydroxylgruppen in dem Polymerisat.

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Polymers and Copolymers of o-Acetoxystyrene and o-Hydroxystyrene[1]

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The fact that the polymer obtained from p-tert-butylphenol and acetylene in the presence of zinc naphthenate acted as a tackifier for GR-S (1-6) suggested to us that a copolymer of o-hydroxystyrene and butadiene might have enough tack so that it could be used to improve the butadiene-styrene copolymer.

o-Hydroxystyrene was prepared from o-coumaric acid by the method of Fries and Fickewirth (7). This monomer was polymerized to a yellow solid by the action of a little benzoyl peroxide and exposure to ultraviolet light. Viscosity measurements indicate that this material is more highly polymerized than the dimer reported by Fries and Fickewirth (7). The infrared spectrum[2] of this polymer showed a band at 3375 cm.$^{-1}$ indicative of the phenolic hydroxyl groups and no appreciable absorption for a carbon-carbon double bond (Figures 1a-1b).

Attempts to copolymerize o-hydroxystyrene with butadiene in the GR-S recipe (8), in a Redox recipe (9), and in a modified GR-S recipe with dodecyl amine hydrochloride as the emulsifier (10) were all unsuccessful.

o-Acetoxystyrene was prepared from o-hydroxystyrene by treatment with acetic anhydride (11), and it too failed to polymerize or copolymerize with butadiene in the GR-S type systems. Apparently, hydrolysis occurred to produce enough inhibitor to stop the polymerization. The residue in the distilling flask when acetoxystyrene was distilled did set to a hard, light yellow polymer which had a molecular weight of approximately 46,000.

A terpolymer of o-acetoxystyrene, styrene, and butadiene was obtained by treating a carbon tetrachloride solution of the three monomers with stannic chloride at 50°. A low molecular weight ($[\eta] = 0.291$) benzene-soluble polymer was obtained. This terpolymer gave characteristic infrared bands for phenyl groups at 3058, 1603, 1505, and 1493 cm.$^{-1}$ and a strong carbonyl band at 1765 cm.$^{-1}$ indicating that the o-acetoxystyrene unit was present in the polymer (Fig. 2).

This terpolymer was hydrolyzed by boiling its dioxane solution with a little hydrochloric acid for several hours. The hydrolyzed

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] We are indebted to Agatha R. Johnson for these infrared spectra.

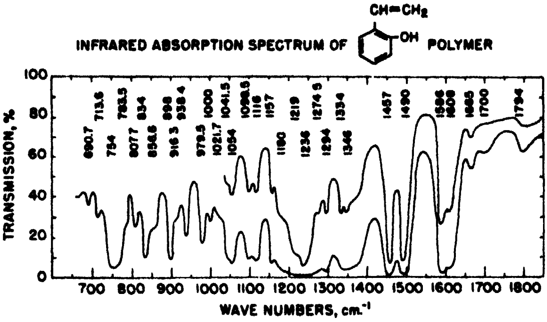

Figure 1a

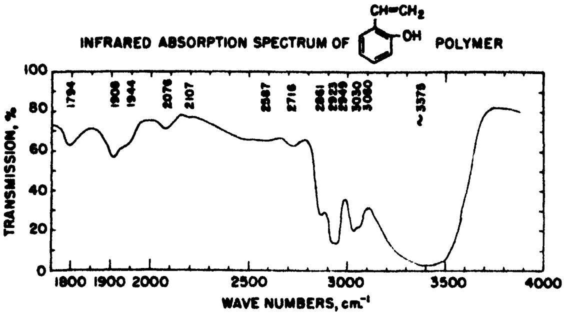

Figure 1b

polymer was isolated by precipitation with methanol. The hydrolyzed polymer was also soluble in benzene ($[\eta] = 0.33$). The infrared spectrum of the hydrolyzed polymer had a strong band at 3450 cm.$^{-1}$ which is characteristic of the hydroxyl group (Fig. 2). This sample of terpolymer was tested as a tackifier for GR-S by Dr. R. F. Dunbrook of The Firestone Tire and Rubber Company and was found to have a zero rating as compared to a value of 10 for Koresin[1].

EXPERIMENTAL

o-Hydroxystyrene

The sample used boiled at 100° at 1 mm.; $n^{27.5}D$, 1.5783; $d_4^{25.5}$ 1.0293.

Analysis.[2] Calcd. for C_8H_8O: C, 79.97; H, 6.71. Found: C,79.68; H, 6.91.

o-Acetoxystyrene

Thirty grams of o-hydroxystyrene was treated with 51 g. of acetic anhydride and 20.7 g. of anhydrous sodium acetate as described by Carr (11). The product weighed 17.5 g. (37%) and boiled at 97-98° at 7 mm.; $n^{20}D$, 1.5324 and d_4^{20} 1.0679. Carr (11) reports b.p. 67-69° at 5 mm.

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[1] We are indebted to Dr. Dunbrook for his permission to quote these results. See Smith, Ambelang, and Gottschalk, Ind. Eng. Chem., 38, 1166 (1946).

[2] Analyses by Clark Microanalytical Laboratory, Urbana, Illinois.

Analysis. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.21. Found: C, 73.65; H, 6.32.

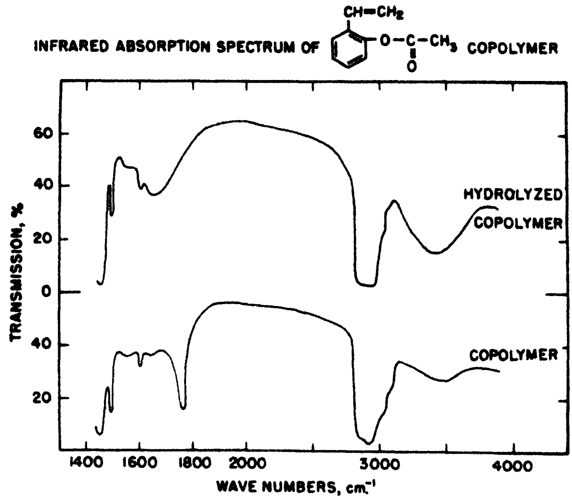

Figure 2

Poly-o-hydroxystyrene

To a 13.5-g. sample of freshly distilled monomer was added a few crystals of benzoyl peroxide, and the solution was irradiated with ultraviolet light for twenty-two days. The highly viscous material thus formed was soluble in benzene, chloroform, methanol, acetone, dioxane, and diethylene glycol, but very sparingly soluble in carbon tetrachloride. A solution in methanol was slowly added to water and a solid polymer was precipitated.

Analysis. Calcd. for $(C_8H_8O)_n$: C, 79.97; H, 6.71. Found: C, 81.24; H, 6.50.

$[\eta]$, 0.43 (in benzene). If one uses the constants for styrene in the Flory (12) equation, this indicates a molecular weight of about 65,000.

Poly-o-acetoxystyrene

The residue in the distilling flask after distilling the o-acetoxystyrene was viscous, and on standing for a week it turned to a light yellow solid which was soluble in chloroform and acetone. A 5-g. sample was dissolved in 50 cc. of chloroform and poured into 500 cc. of methanol. The powdery polymer which precipitated was filtered and dried.

Analysis. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.21. Found: C, 72.85; H, 6.21.

$[\eta]$, 0.35 (in chloroform solution). This indicated a molecular weight of about 46,000.

Attempts to Copolymerize o-Hydroxystyrene with Butadiene in GR-S Type Systems

An emulsion prepared from 1 g. of Rubber Reserve soap, 33 cc.

of water, 0.06 g. of potassium persulfate, 0.1 g. of dodecyl mercaptan, 2 g. of o-hydroxystyrene, 3 g. of styrene, and 15 g. of Phillips research grade butadiene was shaken for two hundred and six hours at 50°, but no polymer was formed. Using the same emulsion except reducing the o-hydroxystyrene to 0.2 g. and increasing the styrene to 4.8 g. gave the same result. When 0.02 g. of o-hydroxystyrene and 4.98 g. of styrene were used, a conversion of 32% in twenty-one hours was achieved, but the product was apparently GR-S.

When a redox system of Rubber Reserve soap 1 g., benzoyl peroxide 0.05 g., ferrous sulfate ($FeSO_4 \cdot 7H_2O$) 0.1 g., sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$) 0.6 g., water 40.0 g., o-hydroxystyrene 1.0 g., styrene 4.0 g., and butadiene 15 g. was shaken for one hour at 50°, no polymer was produced.

Experiments with a system of dodecylamine hydrochloride 1.0 g., water 40 g., potassium persulfate 0.06 g., dodecyl mercaptan 0.06 g., aluminum chloride 0.02 g., o-hydroxystyrene 1.0 g., styrene 4.0 g., and butadiene 15 g. at 30° for twenty-four hours also gave no polymer.

Copolymerization of o-Acetoxystyrene, Styrene, and Butadiene

A solution of 2 g. of stannic chloride, 4 g. of styrene, 1 g. of o-acetoxystyrene, and 15 g. of butadiene in 10 g. of carbon tetrachloride was placed in a 4-ounce screw-capped polymerization bottle. The bottle was rotated end-over-end in a 50° constant temperature bath for forty-eight hours. At the end of that time the contents of the bottle were slowly poured into 500 cc. of methanol. A white rubbery polymer was obtained in 75-80% conversion. The solubility in benzene was 94-99% (static method). $[\eta]$, 0.296 (in benzene). The infrared absorption spectrum of this polymer is shown in Figure 2.

Analysis. Found: C, 81.79; H, 8.95: ash, 1.43.

Hydrolysis of the Terpolymer of o-Acetoxystyrene, Styrene, and Butadiene

A solution of 10 g. of the above polymer in 700 cc. of dioxane was placed in a flask equipped with a reflux condenser and heated to gentle boiling by an oil bath.

Three 10-cc. portions of 10% hydrochloric acid were added at fifteen minute intervals, and the refluxing was continued for ten hours. About half of the dioxane was then removed by distillation under slightly reduced pressure. The remaining hot solution was poured into 800 cc. of methanol, and the rubbery polymer which separated was dissolved in chloroform and the polymer reprecipitated by pouring this solution into excess methanol. The yield of polymer (dried in a desiccator) was 4.5 g. The solubility in benzene was 92-97% (static method). $[\eta]$, 0.33 (in benzene). The infrared pattern is shown in Figure 2.

This polymer did not increase the tack of GR-S when the two were milled together.[1]

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[1] We are indebted to Dr. Dunbrook for his permission to quote these results. See Smith, Ambelang, and Gottschalk, Ind. Eng. Chem., 38, 1166 (1946).

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Synopsis

o-Hydroxystyrene did not copolymerize with styrene and butadiene in GR-S-type systems. A terpolymer of these three monomers was obtained by copolymerizing o-acetoxystyrene, styrene and butadiene in carbon tetrachloride solution by the action of stannic chloride followed by hydrolysis of the acetate groups in the polymer with dilute hydrochloric acid in dioxane solution. The polymer thus obtained did not improve the tack of GR-S.

Résumé

L'orthohydroxystyrène ne copolymérise pas avec le styrène et le butadiène dans la technique habituelle du GR-S. Un polymère ternaire au depart de ces trois monomères a été obtenue par copolymérisation du orthoacétoxystyrène, du styrène et du butadiène en solution dans le tétrachlorure de carbone, par l'action du chlorure d'étain tetravalent, et saponification ultérieure des groupes acetylés du polymère par l'acide chlorhydrique dilué en solution dans le dioxane. Le polymère ainsi obtenue n'améliore pas "tack" du GR-S.

Zusammenfassung

Orthohydroxystyrol formte keine Mischpolymerisate mit Styrol und Butadien in GR-S artigen Systemen. Ein Mischpolymerisat dieser drei Monomere wurde dadurch erhalten, dass eine Loesung von Orthoazetoxystyrol, Styrol und Butadien in Chlorkohlenstoff erst mit Zinnchlorid behandelt wurde und die Azetatgruppen dann in Dioxanloesung mit verduennter Salzsaeure hydrolisiert wurden. Das so erhaltene Polymerisat verbesserte nicht die Klebrigkeit von GR-S.

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Estimation of Crystallinity of Some Polymers from X-Ray Intensity Measurements[1]

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1. INTRODUCTION

In previous papers (1,2) we have reported on crystallinity determinations in cellulosic objects by means of x-ray measurements. The technique applied was essentially that introduced by Goppel in his crystallinity determinations of rubber (3). We copied his method to measure the total amount of radiation involved in each exposure, but introduced certain refinements (use of strictly monochromatized radiation, correction for incoherent radiation).

It seemed of interest to investigate whether examination of a rubber sample according to our procedure would reproduce Goppel's results and, furthermore, whether the method holds some promise for other polymers as well.

The present paper deals with a preliminary exploration in that line. It was also undertaken in view of obtaining some comparative data on the course of the diffusely scattered radiation in polymers other than cellulose which we felt might help us to a better understanding of certain unclarified details observed in the case of cellulose. The investigation of entirely "amorphous" polymers and liquids was also part of this program, but this part of the subject will be deferred to a later paper. The purpose of this publication is merely to draw the attention of other workers to the possibilities for the investigation of other partly crystalline polymers.

2. RECAPITULATION AND DISCUSSION OF THE METHODICAL PRINCIPLE

The principle of Goppel's method in determining the crystallinity in rubber was to measure the background intensity of a partly crystalline rubber sample at a suitable diffraction angle where no diffraction due to the crystalline component occurs, and then to measure the intensity at the same angle for a noncrystalline ("hundred per cent amorphous") sample of the same substance. The ratio of the two values would then give the fraction of the amorphous component in the partially crystallized sample. This is illustrated by Figure 1, where a fictitious example of a radial photometer curve is presented showing some crystalline peaks superimposed on a diffuse background. In this case the intensity qr at the diffraction angle $2\theta = \alpha$ is measured. If the broken line represents the corresponding photometer curve of the same substance in the noncrystalline state, then qr/pr gives the amorphous fraction in the partially crystalline object. The procedure implies that α be so chosen that no crystalline peaks can be expected at this place and that the substance can be easily obtained in the noncrystalline condition. At first sight one might expect that the background of the partially crystalline sample could be found by extrapolating its observed initial part at low angles to higher angles, assuming that the ratio of its intensity at these higher angles with respect to the curve of the 100% amorphous sample remains constant. The hatched area would then represent the integrated intensity of the radiation selectively diffracted by the crystalline portion. However, for theoretical as well as for empirical reasons (see below) this extrapolation is not justified at high angles of diffraction. Even if no crystalline peaks occur at high angles such as β in Figure 1 it will not be allowed to repeat the procedure applied at $2\theta = \alpha$ also at $2\theta = \beta$. The background intensity at such higher angles as β may even be, as we found, practically equal for the crystalline and for the noncrystalline sample. One is, therefore, confronted with the difficulty that the permissibility of the procedure may depend on the correct choice of the angle α.

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[1] Communication No. 57 from the Laboratory for Cellulose Research of the AKU and affiliated Companies, Utrecht, Holland.

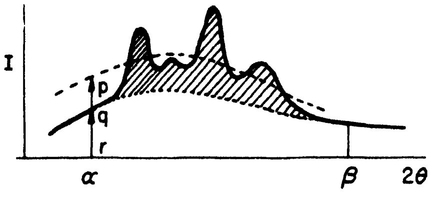

Fig. 1. Fictitious example of the radial photometer curve of the x-ray diagram of a polymer.

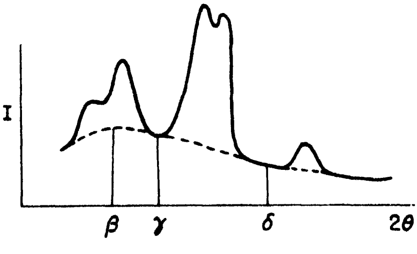

Fig. 2. Another fictitious curve.

In an assumed case, such as shown in Figure 2 where crystalline peaks appear even at low diffraction angles, it may be difficult or impossible to trace the true course of the background, and only if there is a sufficiently large gap between two peaks, as at the angles γ and δ, may one hope that the minimum occurring there will be a reliable guide for tracing the background line. However, it then remains a matter of speculation as to whether the relevant angle is still small enough to permit application of the procedure referred to above.

In the case of cellulose we were faced with a similar case. Here we have ventured to consider the maximum height of the background (angle β in Fig. 2) as a correct measure of the disordered fraction (1,2). Moreover, in cellulose the 100% amorphous representative is not available. The selective diffraction by the crystalline portion (hatched area in Fig. 1) was therefore also measured and the final results were computed from the ratios between the relative values obtained for the crystalline and amorphous fractions in samples of greatly different crystallinity. The agreement with the values deduced from other physical evidence (1) seems to justify the followed procedure with a fairly high degree of probability.

It is clear that in every single case the most suitable procedure for estimating the degree of crystallinity should be scrutinized. The present investigation offers some data which may be of help in other cases.

3. REDUCTION OF INTENSITY DATA OBTAINED FROM DIFFERENT SUBSTANCES TO A COMPARABLE MEASURE

Since it was our aim to compare the diffraction behavior of different polymers, the observed data should be reduced to comparable scale. In this section we shall show how this can be done.

The samples were x-rayed either in the form of cylindrical objects or in the form of approximately plane parallel plates. The dependence of absorption on the angular diffraction could be neglected for the present purpose (1). The pin-hole system had a diameter of 0.8 mm. and the entire primary beam passed through the sample. Its intensity (after absorption) was measured with the Goppel device (1). Let:

I = the intensity of the beam after absorption in the sample.
I_0 = the intensity of the primary beam.
I_c = the intensity of the comparison interference within the Goppel device.
μ_m = the mass absorption coefficient of the substance calculable from its atomic composition.
μ = its linear absorption coefficient.
ρ = its density.
d = the layer of substance (in centimeters) traversed by the primary beam.

The value of the absorption $I/I_0 = e^{-\mu d}$ was always experimentally determined as earlier described (1) and the value of μd calculated. Since $\mu_m \rho d = \mu d$, the value of ρd could also be calculated. If samples of the same substance but of different thickness are now to be compared, the intensity values measured can all be reduced to a given value of ρd for which we have arbitrarily chosen the ρd value of our standardized cellulose pellets from earlier work (1), which amounted to 0.122 (corresponding to a layer of air-dry cellulose 0.084 cm. thick having a density of 1.48). Furthermore, all observations were reduced to the value $I_c = 100$ of the comparison interference.

Hence, if for a given object the values of I_c and ρd were determined, the observed intensities in its x-ray diagram were multiplied by $0.122/I_c \rho d$ in order to reduce them to equal mass and equal intensity of radiation. The total integrated intensity $I_{tot.}$ of all radiation scattered within the chosen range of angular dispersion (2θ from 7° to 42°) was then always constant within experimental error. This constancy is a check on the observations made.

In order also to standardize intensity measurements obtained from different substances the following procedure was followed.

The atomic structure factors of the coherent radiation and its dependence on the diffraction angle were taken from tables given by Compton and Allison (4) for each atom involved (C, H, O, and N). The squares of these values (which are proportional to the intensity) were plotted against 2θ and graphically integrated for the angular range concerned.

In order to find the atomic components of the incoherent radiation intensity, the squares of the structure factors (also tabulated by Compton and Allison) were subtracted from the atomic number. The values so obtained were also plotted against 2θ and graphically integrated. In this way the following atomic intensity factors (given in arbitrary units) were found:

	C	H	O	N
Coherent radiation.....	325	9.6	818	540
Incoherent radiation...	53	10.9	56	53
Total radiation........	378	20.5	874	593

For every substance $C_pH_qO_rN_s$ a reduction factor for total radiation $R_{tot.}$ and for incoherent radiation R_i was calculated as follows:

$$R_{tot.} = (378p + 20.5q + 874r + 593s)/M$$

$$R_i = (53p + 10.9q + 56r + 53s)/M$$

where M is the molecular weight.

Table I. Reduction Factors R_{tot} for Total Radiation and R_i for Incoherent Radiation and Mass Absorption Coefficients μ_m for Various Substances

Material tested	$R_{tot.}$	R_i	μ_m
Cellulose ($C_6H_{10}O_5$)..................	42	4.38	7.78
Cetyl alcohol ($C_{16}H_{34}O$)..............	31	5.2	4.4
Carbon (C)......	32	4.4	4.52
Sugar ($C_{12}H_{22}O_{11}$)....................	42.8	4.36	7.95
Methyl methacrylate ($C_5H_8O_2$)..........	38	4.64	6.3
Rubber (C_5H_8)........................	30.3	5.18	4.02
Bakelite resin.......................	34	4.51	5.05
Paraffin ($C_{25}H_{52}$) Polythene (C_nH_{2n})	30	5.41	3.9
Water................................	50.8	4.33	10.85
Hexamethylene sebacamide ($C_{16}H_{30}O_2H_2$)	31	5.2	4.4

In this way the factors listed in Table I were computed and used for the standardization of intensity data from different substances. In the last column of the table the calculated mass absorption coefficients μ_m are also added. Apart from the substances referred to in this paper some others which will be referred to later on have been included in the table. Standardization of observed intensity data from different substances on the basis of the standard sample dimensions referred to above and cellulose as a standard substance, was performed by multiplying the intensities with 0.122 x $42/I_c\ \rho dR_{tot.}$, where 42 is the $R_{tot.}$ value for cellulose.

The correction for incoherent radiation (see ref. 1), which was experimentally determined from diagrams of sugar single crystals, was reduced on basis cellulose according to the same formula after substituting $R_{tot.}$ by R_i.

Though some objections could be raised against this procedure because it was applied to but a limited range of 2θ values, the experimental data showed that it must be approximately correct for the kind of substances under consideration, since, in all the cases investigated, the value of the total integrated radiation between $2\theta = 8°$ and $2\theta = 42°$ appeared to be constant within about 10% (and usually less). This is also roughly conforming with the experimental error for a single observation.

In this way various photometer curves can be drawn to comparable scale and this has proved to be valuable in a comparative study of certain details.

4. RAW RUBBER

The rubber sample investigated was from a sheet of Hevea crepe rubber stored for 33 years and obtained by courtesy of Prof. A. Van Rossem, Delft. Its density was 0.9471 at 20° and 0.9185 after melting (warming up to 80° and cooling to room temperature). The sample was x-rayed at 18°C. in the condition in which it was received and afterwards while kept at a temperature of 50°C. The value of ρd determined from absorption was 0.149.

Figure 3A shows the two standardized photometer curves obtained. The values of $I_{tot.}$ found (i.e., the total integrated intensities on standard basis) were 4.3 and 4.4^5, respectively, which check very well with the value of 4.4 previously found for cellulose (1). As previously stated, this demonstrates the correctness of the reduction factor given in Table I.

Following Goppel's procedure, the amorphous fraction in the partially crystalline sample was computed from qr/pr at $2\theta \sim 11°$, after subtraction of the height of the incoherent background at that angular dispersion (the incoherent background is shown by the hatched area in Figure 3). Correction for radiation diffracted by air was, of course, also made (see ref. 1).

The crystallinity following from this is 0.45 with correction and 0.40 without correction for incoherent radiation. This figure is rather considerably higher than that found by Goppel on the same sample (0.23) who used ordinary filtered copper radiation and no correction, but not too different, from that found by Arlman (5), who recently repeated Goppel's work using monochromatic radiation and also accounting for incoherent radiation.

The broken line in Figure 3 gives the extrapolation of the "amorphous background" for the partially crystalline sample, representing the intensities of the curve of the molten sample multiplied by 0.60 (uncorrected value of the amorphous fraction). The area between this curve and the observed one with the crystalline peaks then would represent the radiation diffracted by the crystalline fraction. However, this will only be true at not too large angles of diffraction. Beyond $2\theta = 30°$ it becomes doubtful whether this area may be thus interpretated, since there are no more peaks detectable and since the curve of the entirely amorphous sample and that of the partially crystalline sample practically coincide. This is still better demonstrated by Figure 3B giving this part of the films photometered with a higher sensitivity. (The dotted curve in this figure is also drawn more correctly as 0.45 of the corrected height of the 50° curve).

At higher values of 2θ the background intensity is independent of the degree of crystallinity. Both the crystalline and amorphous fractions contribute to it.

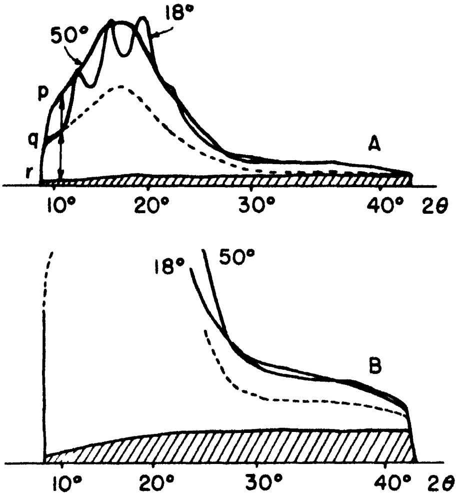

Fig. 3. Standardized photometer curves of the patterns of raw rubber at 18° and 50° (hatched area equals incoherent radiation). Part B represents the lower portion of part A, taken with higher sensitivity.

5. POLYTHENE

Polythene taken from a commercial film was introduced into a very thin-walled capillary (inner diameter 1.5 mm.) and fused under vacuum at a temperature of 135-140° to completely fill the bottom part of the capillary. Then the capillary was cooled slowly to room temperature. Monochromatic x-ray photographs were taken according to our standard procedure at 18, 90, 115, and 135°. (The melting point of polythene lies at about 120°). Afterwards, the capillary was cleaned and the empty capillary was x-rayed at the same spot.

The absorption factor, exp. $-\mu d$ was 0.177 for the capillary with polythene and 0.40 for the empty capillary. From this follows that for the polythene alone $\mu d = 0.810$ and $\rho d = 0.208$.

The photometer curve from the empty capillary (diffraction by the glass) was subtracted from those of the polythene plus glass curve accounting for the various I_c values observed. The values of the total diffracted intensities $I_{tot.}$ between $2\theta = 7°$ and $2\theta = 42°$, standardized according to the procedure indicated in section 3, were found to be 4.25, 4.15, 4.3, and 4.3, respectively, again in satisfactory conformity with the value found for cellulose.

As known from the work of Bunn and Alcock (6) the crystalline pattern of polythene gradually disappears on heating to finally make place for a diagram similar to that given by other liquids and showing a broad band with a maximum corresponding to a Bragg angle slightly smaller than that of the most intense line (110) of the crystalline pattern.

Figure 4A shows the standardized photometer curves of the polythene taken at 18° and at 135°; Figure 4B shows for comparison the curve at the intermediate temperature of 90°. In Figure 4A it is seen that the intense 110 peak occurring in the diagram taken at 18° is substituted by a much broader band in the 135° diagram and the maximum of this band lies at a smaller 2θ value. In the diagram taken at 90° (Fig. 4B) the 110 line and the band both have an appreciable intensity and they are not resolved but merge.[1]

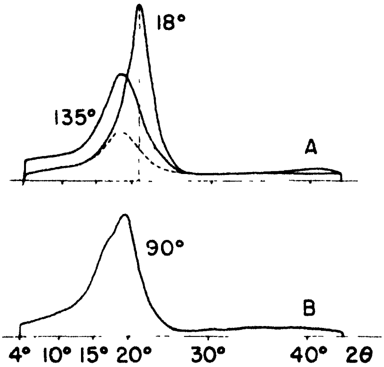

Fig. 4. (A) Standardized photometer curves of polythene at 18° and 135°. (B) The same at 90°.

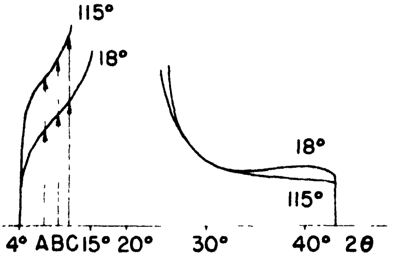

Fig. 5. Curves from Figure 4A enlarged (taken with higher sensitivity of the photometer).

It is also seen in Figure 4A that at small angles the background of the 135° photograph is more intense than that in the 18° photograph. The 90° photograph is, in this respect, intermediate between the two. On the other hand the background at higher angles beyond the peaks is sensibly equal at all temperatures. At about $2\theta = 40°$ only, the 18° curve rises slightly above the 135° curve (compare also the enlarged picture in Figure 5). This is conceivable since in this region crystalline polythene yields some weaker lines (020 among others; see the paper of Bunn and Alcock) which are, of course, present only in the crystalline specimen.

Thus we see that, just as in rubber, the gradual disordering taking place with rise in temperature does not express itself in the background intensity at angles larger than about $2\theta = 30$.

Now if we venture to consider the liquid polythene at 135° as being in a completely disordered state and to take the intensity of the background at small angles, for instance, between $2\theta = 7°$ and 11° as a measure of the disordered or "amorphous" fraction, then we can use an analogous procedure to determine its percentage in the partially crystalline states as that applied in rubber.

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[1] For reasons earlier outlined (1) our procedure gives rise to a rather considerable apparent broadening of x-ray lines (which is however irrevalent for the present purpose). The merging of the 110 line and the band is therefore accentuated.

This has been done with the aid of photometer curves taken with higher sensitivity. The relevant 18° and 115° curves are reproduced in Figure 5. The heights of all the curves were measured at the points indicated by A, B, and C lying at 2θ 8°5 , 10°5, and 12°, respectively. Taking into account the corrections for incoherent radiation (which were very small only in this region) this yielded the following figures for 1-x and x (where x is the crystalline fraction).

TABLE II. Values of (1-x) and x in Polythene from X-Ray Diagram

Temperature, °C.	(1-x) A	(1-x) B	(1-x) C	(1-x) Average	x
18	41^5	48	47	46	54
90	75	78	-	76^5	23^5
115	86	91	100	92	8
135	100	100	100	100	0

In Table III the average x values found are listed together with the estimates of Raine, Richards, and Ryder (7) from heat capacity measurements and with those from Hunter and Oakes (8) from density measurements at different temperatures. The agreement is as yet not very satisfactory and more work will be necessary in order to know which figures are nearest to the truth.

TABLE III. Comparison of x Values for Polythene Found by Different Methods

Temperature, °C.	X-rays	Heat capacity	Density
18	54	76	55
40	--	75	55
60	--	70	55
90	23^5	51	45
110	--	17	25
115	8	0	10

It is of interest to study another feature of Figure 4A more closely. If the fraction of disordered substance in the 18° sample is actually 0.46 and if its state of order be the same as that in the entirely molten polymer, we can determine its share in the scattering of x-rays by drawing a curve having the same shape as the 135° curve but at an intensity level 0.46 times lower. This curve is represented by the dotted line in Figure 4A. We can then, by subtraction of this curve from the 18° curve, find the actual shape of the crystalline 110 peak. The result is shown in Figure 6.[1] It is seen that a very normal and now almost symmetrical curve is obtained, whereas the peak in the 18° curve of Figure 4A is asymmetrical. It would thus seem that the contribution of the disordered portion to the 18° curve actually has the shape as represented by the dotted curve and, on the other hand, this may be regarded as a justification of the applied procedure.

The occurrence of a still rather pronounced maximum in the curve of the liquid polythene as well as in that of the disordered portion of the solid samples indicates that in both there is a certain amount of short range order, quite similar to that present in low molecular liquid substances.

The half width value of the "amorphous band" in the 135° curve is 2.5 times as large as that of the crystalline 110 peak shown in Figure 6. This is of the same order as the bands given by low molecular liquids.

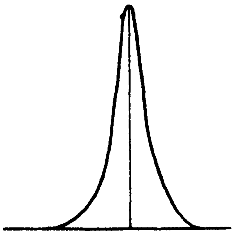

Fig. 6. Shape of the 110 line in the crystalline portion as obtained from Figure 4A by subtraction of the background.

6. PARAFFIN

It seemed of interest to investigate also a low molecular weight paraffin as a counterpart to polythene. To this end we used a commercial paraffin sample melting at 55-60°. The same technique was employed; the paraffin was enclosed in a thin-walled capillary and x-rayed at 18°, 50°, and 65°. The value of ρd (after subtraction of the glass) was 0.116. The $I_{tot.}$ values at 18°, 50°, and 65° were computed to be 4.3, 4.1, and 4.4, respectively.

The three photometer curves are shown in Figure 7.

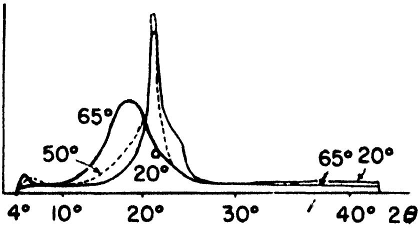

Fig. 7. Standardized photometer curves of a low molecular paraffin (mp. 55-60°) taken at 20° and just below and above the melting point.

It is seen that the transition from the solid to the liquid state involves similar changes in the diagram as observed in polythene. A significant difference with polythene, however, is also detected. At low diffraction angles, in the region between $2\theta = 4°$ and 10°, very little, if any, change in the background intensity is found. In other words, there is a significant difference between the molten polythene and the molten paraffin in this regard.

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[1] Since, at high angles, the background is equal at all temperatures the dotted curve has been also drawn to end at the same height.

The broad band with its maximum at about $2\theta = 18°$, which is present in molten polythene as well as in liquid paraffin, indicates that there is a certain amount of low range order in both liquid substances. Besides, liquid polythene shows a higher degree of disordering reflected by the about four times higher background intensity at low angles.

The broad band is common to low molecular liquids. It is known that the molecules in such liquids are all but randomly arranged. Neighboring molecules do change their relative positions, but on the average they are oriented with respect to each other in a way very similar to that in the crystalline state. From this point of view liquids are not entirely disordered or "amorphous" in the sense likely to be attached to this term in solid polymers. Perhaps we may, in a sense, consider the liquid polymer as a mixture of an "amorphous" and a "liquid" fraction. From this point of view the crystallinity figures computed for the solid polymer as listed in Table III might be too low, since the background at $2\theta = 10°$ of the "hundred per cent amorphous" polymer might still be somewhat higher than that of the molten substance.

7. POLYHEXAMETHYLENE SEBACAMIDE

The investigation was carried out with two samples kindly supplied to us by Dr. C. S. Fuller (Bell Telephone Laboratories, Summit, N. J.). One sample had been rapidly quenched from the melt and the other was a sample annealed for a certain time just below its melting point in order to obtain a maximum degree of crystallization.

The ρd values were determined to be 0.108 and 0.194, respectivly, and the $I_{tot.}$ values of the standardized photometer curves (between $2\theta = 7°$ to $42°$) 4.34 and 4.37. These curves are reproduced in Figure 8 (A_1 and B_1). The difference between the two curves corresponds to the relevant description given by Fuller and co-workers (9).

The quenched specimen shows signs of less perfect order than that present in the annealed sample, the two principal peaks being resolved in the latter only. The small peak at about $2\theta = 13°$ is very weak and has shifted to a lower 2θ value in the quenched sample. This interference corresponds to the distance between the planes in which the hydrogen bonds lie. Whereas a considerable amount of three-dimensional order is indicated by the diagram of the annealed sample, that of the quenched sample is indicative of two-dimensional rather than three-dimensional order. Order in the planes bearing the hydrogen bonds is obviously still well pronounced, but the order in the direction perpendicular to these planes is poor. This is a case similar to that encountered in regenerated celluloses, where order is also confined mainly to the 101 planes in which the hydrogen bonds lie and where "recrystallization" consists mainly of improvement of the ordering perpendicular to these planes (2).

In order to obtain some quantitative idea on the proportion between ordered and disordered substance, one may venture to separate the crystalline peaks from the background as indicated by the broken lines in Figure 8. After subtraction of the correction for air scattering (dotted line) the background shows a flat maximum lying near to the 2θ value of the intense peak.

TABLE IV. Values of I_{cr}, A_m and $I_{tot.}$ for Polyhexamethylene Sebacamide

		I_{cr}	A_m	$I_{tot.}$
A_1	Quenched	187	0.32	4.34
B_1	Annealed	226	0.25^5	4.37
	After Phenol Treatment			
A_2	Quenched	257	0.19	4.00
B_2	Annealed	279	0.21	4.10

Following the method of evaluation applied to cellulose (1,2) we have tentatively taken the height of this maximum (corrected for incoherent radiation) as a relative measure of the disordered fraction and the integrated intensity I_{cr} of the peaks above the background as a relative measure of the ordered fraction (see Table IV).

Fankuchen, Bergmann, and Mark (10) have recently shown that polyamides can be made more crystalline by a treatment with an aqueous phenol solution.

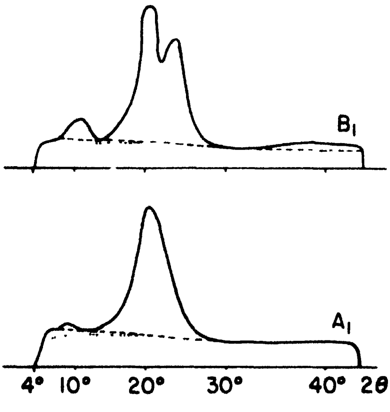

Fig. 8. Standardized photometer curves of a quenched (A1) and an annealed (B1) sample of polyhexamethylene sebacamide.

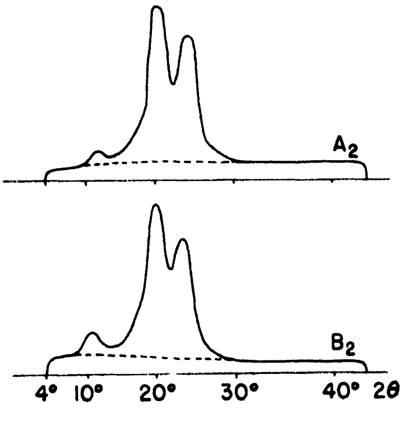

Fig. 9. Standardized photometer curves of the same samples in Figure 8 after treatment with phenol solution.

Figure 9 shows the standardized photometer curves of x-ray pictures taken from the same specimens represented by Figure 8 after treatment for 1 week at room temperature in a saturated phenol solution, then washing away the phenol followed by drying in the air. It is seen that the degree of order is considerably increased in both cases (11). The resolution of the main peaks is now good in either specimen and also the background intensity is smaller than in

Figure 8. In the quenched specimen, however, the small low angle peak is still less intense than in the annealed one.[1] These curves were evaluated as those from Figure 8 (using a curve taken with greater sensitivity for the determination of A_m). The results are listed in Table IV. All figures are calculated for $\rho d. = 0.122$ and $I_c = 100$ on basis cellulose (using the factors given in Table I). In the same way as was done in the case of cellulose, we have ventured to plot these figures in a nomogram and calculate the "crystalline" and "amorphous" fractions from them. The result is shown in Figure 10. If the applied method of evaluation is justified all the points obtained when A_m is plotted against I_{cr} should fall on a straight line. Taking the large experimental error into account (1), this is practically fulfilled by the observations recorded in Table IV. A percentage of crystallinity scale is marked along the straight line from which we see that, according to this method of evaluation, the specimens in question range between 50% and 70% crystallinity.

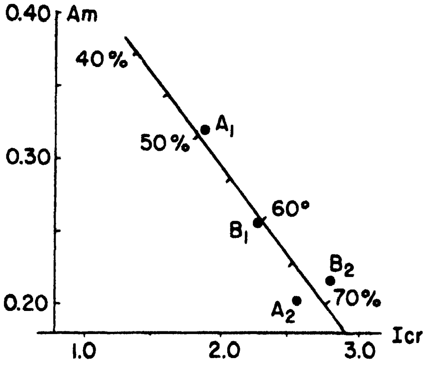

Fig. 10. Crystallinity nomogram for polyhexamethylene sebacamide.

CONCLUSION

The foregoing experiments seem to show that it will be possible for most partially crystalline polymers to get an approximately correct idea of their degree of crystallinity (or, say, degree of ordering) from x-ray measurements performed on a quantitative basis. Though the method of evaluation followed in this paper to express this crystallinity in figures may still give rise to various objections, it has been shown beyond doubt that the background intensity when measured at the proper diffraction angle and the integrated intensity of the crystalline interferences occurring below $2\theta \sim 40°$ (more or less broad as the latter may be) run antiparallel in various samples of a given polymer which, on other grounds, may be regarded as representing specimens with different degree of crystallinity.

As the case of the polyamides and also that of cellulose shows, there is no fixed correlation between the degree of resolution of neighboring interferences or the width of the lines and the total degree of order as derived from the aforementioned data (compare Figures

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[1] It is not clear why the background at high angles is higher in the quenched sample.

8B and 9B). The "sharpness" of an x-ray diagram taken in the common sense does not necessarily give a correct impression of the over-all state of ordering in the sample. The investigation should be supplemented with quantitative studies of the kind treated of in this paper.

In cases where the lattice of the crystalline polymer contains planes in which cohesion is particularly strong (hydrogen bonds), as in cellulose and the polyamides, the interference line corresponding to the spacing between these planes may show considerable variations in intensity and width which are significant in that they reveal important differences in degree of order which are not or much less markedly expressed in the background intensity or in the integrated total intensity of the crystalline peaks. Whereas the latter data stand for the total degree of order, the former is bound up with states of two dimensional order ("two dimensional crystallinity") which seem to play a considerable role in this kind of polymers (see also reference 2).

It is also of interest that the background intensity at higher angles of diffraction ($2\theta > \sim 30°$) is not necessarily correlated with the degree of crystallinity. Marked differences in background intensity found in this region when comparing certain polymers remain to be elucidated.

Finally, we wish to recall that the intensity curves reproduced in this paper refer to a plane film. To reduce them to the case of a cylindrical film the ordinates should be multiplied by $(\cos 2\theta)^{-2}$.

Acknowledgment

The authors are indebted to the Laboratory for Technical Physics of the Technical University at Delft for the use of its x-ray equipment (including a 40 KV-100 mA rotating anode tube) and microphotometer, and to Mr. J. J. Arlman for valuable advise.

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Synopsis

The paper deals with a tentative plan to extend quantitative x-ray measurements for determining the degree of crystallinity of polymers (as used earlier in cellulose determinations), to the investigation of rubber, polythene, and a polyamide. Strictly monochromatized copper radiation was used. The results show that further work along these lines may be promising. The raw rubber sample used was identical with one of those investigated by Goppel and by Arlman. It yielded a crystallinity figure higher than that reported by Goppel, but conformed with that found by Arlman. The figures obtained for polythene at different temperatures are compared with those derived from density and heat capacity measurements by other workers. The degree of crystallinity of polythene at room temperature is found to be $\sim$ 55%, and in samples of polyhexamethylene sebacamide, previously treated in different ways, figures between $\sim$ 50 and 70% are obtained. It is shown that the possibility of using the background intensity as a measure of the disordered fraction is confined to not too high angles of diffraction. A method is described (and experimentally checked) allowing for reducing the curves of intensity distribution as a function of 2θ as observed in various polymers to a comparable scale. It is further emphasized that, in polymers where hydrogen bonds play a decisive role in intermolecular cohesion, the x-ray results suggest that the "crystalline" or ordered fraction may to a considerable extent involve states of two-dimensional order.

Résumé

Cet article a pour but d'étendre les mesures quantitatives aux rayons-x à la détermination du degré de cristallinité des polymères dans l'étude du caoutchouc, du polythène et d'une polyamide (ainsi que cela avait été précédemment utilisé dans le cas de la cellulose). On utilise une radiation du cuivre, strictement monochromatique. Les résultats s'avèrent prometteurs pour un travail ultérieur dans la même direction. L'échantillon de caoutchouc brut examiné était le même que celui étudié préalablement par Goppel et par Arlman. Il a fournit un degré de cristallinité supérieur à celui indiqué par Goppel, mais en accord avec la détermination de Arlman. Les figures obtenues pour le polythène à différentes températures ont été comparées à celles déduites des déterminations de densité et capacité calorifique d'autres auteurs. Le degré de cristallinité du polythène à température de chambre s' élève à 55% environ; dans le cas d'échantillons de polyhexaméthylène-sébaçamide, au préalable traites de différentes façons, on obtient des valeurs de $\sim$ 50 à 70%. On montre que la possibilité d'utiliser l'intensité de l'arrière-fond, comme une mesure de la partie non-orientée, est limitée à des angles de diffraction, pas trop élevés. Une méthode est décrite (après essais expérimentaux) permettant de ramener les courbes de distribution d'intensité en fonction de 2θ à une échelle comparable (observés pour différents polymères). Les auteurs insistent sur le fait que, dans les polymères, ou les liaisons-hydrogène jouent un rôle important dans la cohesion intermoléculaire, les résultats aux

rayons-x suggèrent que la fraction "cristalline" ou ordonnée peut comporter des proportions considérables d'un ordre bi-dimensionel.

Zusammfassung

Plaene, die quantitativen Roentgenstrahlenmessungen zur Bestimmung des Kristallinitaetsgrades von polymeren Stoffen (so wie fuer Cellulose frueher angewandt) fuer Untersuchungen von Gummi, Polyaethylen und eines Polyamids zu benuetzen, werden besprochen. Reine, monochromatische Kupferstrahlung wurde benuetzt. Die Ergebnisse zeigen, dass weitere Arbeit in dieser Richtung erfolgreich sein duerfte; die benuetzte Rohgummiprobe war gleich denen, die von Goppel und Arlman untersucht wurden. Ein hoeherer Kristallinitaetsgrad wurde erhalten, als der von Goppel berichtete; die Ergebnisse stimmten aber mit denen von Arlman ueberein. Die Resultate fuer Polyaethylen bei verschiedenen Temperaturen werden mit den Resultaten anderer Forscher, von Dichte und Waermegehalt abgeleitet, verglichen. Der Kristallinitaetsgrad von Polyaethylen bei Raumtemperatur ergab sich als ~ 55%, und in Proben von Polyhexamethylen-Sebacinamid, die vorher in verschiedener Art behandelt wurden, ergaben sich Resultate von ~ 50-70%. Es wird gezeigt, dass die Moeglichkeit, die Hintergrundsintensitaet als ein Mass der disorientierten Fraktion zu betrachten, auf nicht zu hohe Diffraktionswinkel begrenzt ist. Eine Methode wird beschrieben (und versuchsweise geprueft) durch welche die Intensitaetsverteilungskurve als Funktion von 2θ, wie in den verschiedenen Polymerisaten beobachtet, in einem vergleichbaren Masstabe dargestellt werden kann. Es wird betont, dass bei Polymerisaten, in denen Wasserstoffbindungen in der intermolekularen Cohaesion eine entscheiden de Rolle spielen, die Roentgenstrahlenresultate darauf hinweisen, dass die "krystallinische" oder geordnete Fraktion groesstenteils zweidimensionale Ordnung darstellt.

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Ultraviolet Absorption Spectra of Some Copolymers Containing Acenaphthylene, and of Related Compounds

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The composition of the copolymers of styrene and acenaphthylene cannot be determined accurately from combustion data because of the close similarity in the elementary composition of styrene (92.3% carbon) and acenaphthylene (94.7% carbon). In this respect the system resembles the styrene-butadiene copolymers. However, it has recently been shown that measurements of the ultraviolet absorption spectra of copolymers of styrene and butadiene can be used to determine the concentration of one of the components (1-3). The p-chlorostyrene system permits of a direct comparison of the spectrophotometric and chlorine analysis methods and the results were found to be in good agreement, thus justifying the basic assumption that in these two systems the specific extinction coefficient of the copolymer at a certain wave length varies linearly with the percentage of styrene (or p-chlorostyrene).

Previously Smakula (4) had concluded that the absorption of light in the near ultraviolet by polystyrene samples of different molecular weight is due to the presence of benzene rings and there is virtually no interaction between different benzene rings, i.e., the system behaves in this respect as if it were nonconjugated. Close inspection of the spectra of the copolymers of styrene and butadiene, however, reveals that they do not conform exactly with those which would result from the simple superposition of the spectra of polystyrene and polybutadiene (1). This leads to some uncertainty in the measurement of the styrene content of the copolymers by the ultraviolet absorption method, but the error is of a low order, being less than 3%. The observed slight shift of the wave length of maximum absorption (~ 2 mμ) for the copolymers with respect to polystyrene affords qualitative spectroscopic evidence for the formation of a true copolymer.

We have observed that the spectra in the wave length region 280-330 mμ of certain copolymers of acenaphthylene with styrene when compared with the spectra of polyacenaphthylene and polystyrene indicate the formation of a true copolymer. The spectra of the copolymers containing a small percentage of acenaphthylene differ so completely from those of polyacenaphthylene and polystyrene that it is difficult to estimate the polyacenaphthylene contents by direct matching of the spectra with that from polyacenaphthylene in the manner previously used by one of the authors (5) for a different purpose.

The absorption in the wave length range 280-330 mμ arises from the acenaphthylene nucleus. The important observation was made that the spectra in this wave length region of the copolymers containing approximately 10% acenaphthylene and 90% styrene is practically identical with that exhibited by the copolymer in which the styrene is replaced by methyl methacrylate. This is consistent with the view that the observed absorption spectra arises from acenaphthylene groups interacting amongst themselves and not from interaction between acenaphthylene and styrene or acenaphthylene and methyl methacrylate groups.

Under certain conditions (e.g., in the presence of acids) acenaphthylene shows a strong tendency to polymerize to the dimer (biacenaphthylidene), thus differing in behavior from styrene. Since it was thought possible that this tendency of the acenaphthylene groups to unite in pairs might persist in the copolymers, the spectra of the copolymers have been compared with the spectra of the two forms of 1,1'-biacenaphthyl. The general resemblance between the spectra of the copolymers containing a small percentage of acenaphthylene and one of the biacenaphthyls is remarkable. This resemblance may be a result of the tendency of acenaphthylene groups to occur in pairs in the copolymers.

EXPERIMENTAL

The acenaphthylene was prepared by the dehydrogenation of acenaphthene (6), while the styrene and methyl methacrylate monomers were distilled from commercial samples.

The polymers and copolymers of acenaphthylene (6) were prepared by thermal treatment. Molten acenaphthylene and solutions of acenaphthylene in styrene were sealed in evacuated tubes and maintained in an oil thermostat at 97 °C. for periods of three to four days. In some cases polymerization was initiated by adding 0.5% by weight of benzoyl peroxide. In all the cases the polymerization was carried to as near completion as possible so that the composition of the polymer approximates to that of the initial monomer mixture. Since unreacted acenaphthylene monomer imparts a yellow colour to the solid polymers and interferes with the measurement of the absorption spectra of the polymers, the product was freed from unreacted monomers by repeated dissolution in benzene followed by precipitation by a large volume of methyl alcohol.

The preparation of the two forms of 1,1'-biacenaphthyl will be described by one of us (7) elsewhere. As the molecule contains two asymmetric carbon atoms, presumably one form corresponds to the racemic mixture and the other corresponds to the meso form. Here the two forms will be referred to only by the melting points, which are 168.5°C. and 120°C.

A pure sample of benzene (at least 99.9% pure by freezing point) was used as the solvent in the measurement of the absorption spectra. This hydrocarbon absorbs strongly at wave lengths below 275 mμ but can be used as a solvent at a path length of 1 cm. for the range 280-330 mμ .

Originally the spectra were obtained by means of a Hilger medium quartz spectrometer, using a variable path length cell and a hydrogen lamp as light source. In this way the spectra of two solutions could be recorded adjacent to each other and so a direct comparison could be made. Subsequently a Hilger Spekker Photometer was used in conjunction with a Hilger Large Quartz Spectrograph. The results of these studies have been confirmed and extended by additional measurements with a quartz Beckman Spectrophotometer and the curves recorded in this paper were obtained with this instrument.

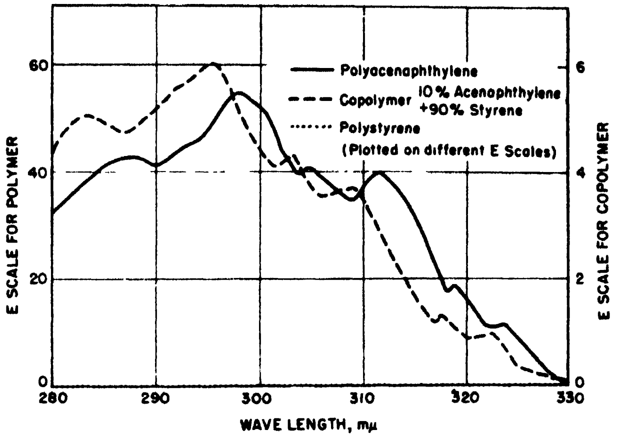

Fig. 1. Comparison of spectra of polyacenaphthylene and polystyrene with that of the 10% copolymer.

RESULTS

Although there were slight differences in molecular weight between the catalyzed and uncatalyzed preparations, the former exhibiting lower values, yet the spectra were very similar in the range 280-330 mμ. The spectra of the uncatalyzed samples are the only ones recorded here.

The wave length is indicated in mμ, and, in order to use the same units throughout, the absorption is expressed as the specific extinction coefficient, i.e., by E, where $E = D/cl$, and D is the optical density, c the concentration in grams per litre, and l the path length in centimeters.

Figure 1 contains the curves for polyacenaphthylene, polystyrene, and copolymer containing 10% of acenaphthylene with styrene. All percentages are on the weight basis of the monomers before polymerization. To facilitate comparison of the curves different scales for E have been used for the polymers and copolymers. Obviously the specific absorption coefficient of polystyrene in this range is negligible compared with that of the other polymers.

TABLE I. Comparison of Wave Lengths for Maximum Absorption

Sample	Wave length of absorption maxima						
Polyacenaphthylene	287.5	293.5	298.0	304.5	311.0	318.5	323.5
Styrene-acenaphthylene copolymer (90:10)	283.8	292.3	295.0	303.0	309.0	317.5	322.0
Methyl methacrylate-acenaphthylene copolymer (90:10)	283.8	292.5	295.0	303.0	308.0	317.5	322.0

The spectra of polyacenaphthylene and the copolymers resemble each other in a general way, for example, with respect to the number of maxima and minima and their disposition, but the curves show a marked difference on the wave length scale as indicated in Table I and shown in Figure 1. This shift in the maxima and minima is of such a magnitude in the wave length region 300-350 mμ that many of the peaks in the absorption curves for polyacenaphthylene coincide with the troughs in the curve for the copolymer and conversely. This behavior is very apparent on records obtained when the absorption spectra are photographed in juxtaposition, using a hydrogen lamp as light source.

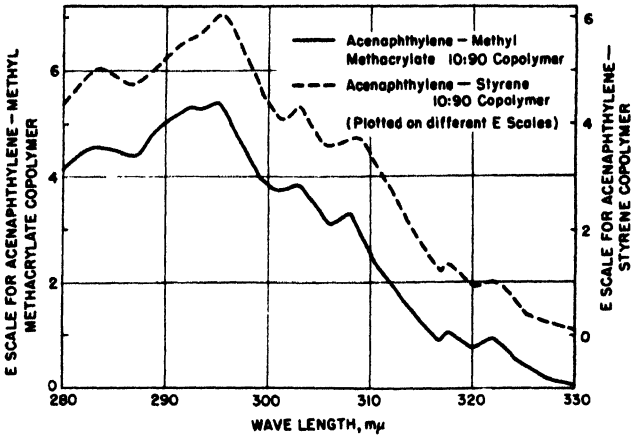

Fig. 2. Spectrum of the copolymer of acenaphthylene with styrene compared with that of the copolymer with methyl methacrylate.

The similarity between the spectra of the copolymers containing methacrylate and styrene is clearly illustrated by Figure 2 where the curves have been plotted on different E scales to avoid confusion. The spectra of samples of copolymer which were rich in acenaphthylene (60%, 80%, or 90%) resemble the curves for polyacenaphthylene and are not reproduced here.

In an attempt to establish the cause of the shift of the maxima in the absorption spectra of the copolymers, the spectra of acenaphthene and the two forms of biacenaphthyl were measured and are shown in Figure 3. These curves together with that of polyacenaphthylene given in Figure 1 represent the spectra of a sequence of molecules with increasing chain length. Similar maxima and minima can be traced throughout this series with the possible exception of the rather flattened peak at 315.5 mμ in acenaphthene.

The similarity between the position of the maxima and minima in the absorption spectra of the two forms of biacenaphthyl was to be expected, but the differences between the relative intensities is peculiar, cf. the bands at 322 which have nearly equal E values with the bands at 295 mμ where the band from the isomer of melting point 168.5°C. is strongest. Other solutions made up from the same samples confirmed this difference when the absorption bands were directly compared. It would thus appear that the ultraviolet absorption spectra of the meso and racemic forms of this compound are different. The resemblance between the spectra of the biacenaphthyl (m.p. 120°C.) and the copolymers will be discussed below.

Figure 4 gives the absorption spectra from 240 to 350 mμ of a benzene solution of acenaphthylene. The intensity and width of the absorption band indicates the desirability of removing unreacted monomer from a polymer before examining its spectra. The only previous publication of the spectra of this compound appears to be the work of Craig, Jacobs, and Lavin (8) on the alcoholic solution.

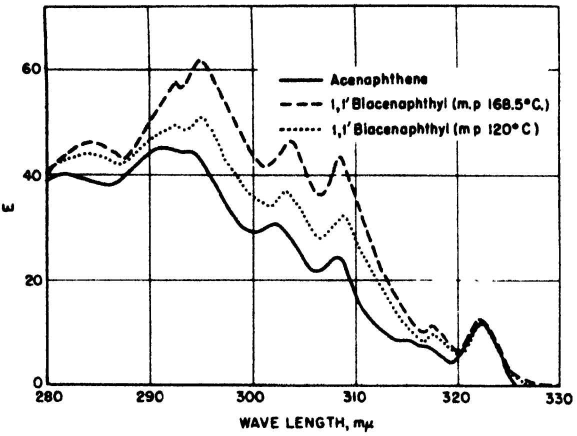

Fig. 3. Spectra of acenaphthene and of the two forms of 1,1'-biacenaphthyl.

TABLE II. Ratio of the Values of E for Corresponding Maxima in the Absorption Curves

(Values at the head of the columns for ratio of E are the wave lengths of the bands compared.)

Substance	$\frac{291}{302}$	$\frac{291}{308}$	$\frac{295}{303}$	$\frac{295}{308.5}$	$\frac{298}{304.5}$	$\frac{298}{311}$	$\frac{295}{322}$
Acenaphthene	1.48	1.84	-	-	-	-	-
1,1'-Biacenaphthyl m.p. 168.5° C.	-	-	1.31	1.42	-	-	4.8
m.p. 120.0° C.	-	-	1.41	1.61	-	-	5.2
Styrene-acenaphthylene copolymer 90:10	-	-	1.40	1.63	-	-	6.0
Methyl methacrylate-acenaphthylene copolymer 90:10	-	-	1.40	1.65	-	-	5.8
Polyacenaphthylene	-	-	-	-	1.34	1.37	-

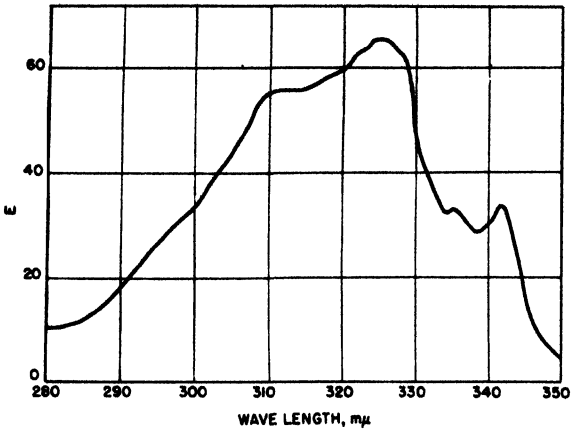

Fig. 4. Spectrum of a benzene solution of monomeric acenaphthylene.

DISCUSSION

As stated in the introduction the similarity between the spectra of the two 10% copolymers with styrene or methyl methacrylate (Figure 2) suggests that these spectra arise from acenaphthylene groups interacting amongst themselves.

In the 10% copolymer with styrene (7.1 mole per cent acenaphthylene) we should expect 86% of acenaphthylene groups to have styrene radicals as nearest neighbors if the radicals combine randomly. Recently a number of papers have been published in which the behavior of monomers in copolymerization have been discussed (9,10). Two main types of behavior have been detected although intermediate forms exist. In one (termed ideal, see Wall (11)), the reactivity is independent of the terminal groups on the radical, while in the other extreme case each radical reacts with the monomer unit of opposite type to the monomer group on the radical (e.g., styrene and methyl methacrylate show some tendency to alternate (12)). If this occurred with acenaphthylene and methyl methacrylate it would be expected that the majority of acenaphthylene groups in the dilute polymers would be sandwiched between methacrylate radicals. If this were the case it would be expected that the spectra of the copolymers would resemble the spectra of acenaphthene rather closely. Actually the observed spectra do not show a very close resemblance, for not only are there differences in the wave lengths of certain of the bands, e.g., the strongest absorption is at 295 mμ for the polymer and 291 mμ for acenaphthene, but also the relative intensities are different as is shown in Table II.

The spectra of 10% copolymers show a marked resemblance to that of the lower melting form of biacenaphthyl both with respect to the position and intensities of the maxima, with the possible exception of the small maxima at 295 mμ , as comparison of Figures 1 and 2 and Table II indicates.

The agreement on the ratios 295/303, 295/308.5 is good, but is not so close for 295/322 although here the accuracy of measurement is probably less because the 322 mμ bands are weaker.

The spectra thus appear to indicate that acenaphthylene groups tend to occur in pairs in the copolymer; however, the differences between the spectra of the copolymer, acenaphthene, and one of the biacenaphthyls may not be sufficient to establish this point, so that additional evidence from other sources will be necessary before this conclusion can be regarded as proved.

Quantitative Analysis of Copolymers

This work was originally undertaken with the object of devising a method of estimating acenaphthylene in copolymers. If complete polymerization of mixtures of the monomers could be achieved, a calibration curve of E for a certain band against acenaphthylene content could be drawn up and this could be used subsequently to determine the percentage of acenaphthylene in an unknown sample. Certain of the mixtures proved difficult to polymerize completely, so that this method was not attempted.

TABLE III. Weight Percentage of Acenaphylene in the Copolymers Calculated from the Absorption Spectra and Compared with Original Monomer Concentration

Wt. % of acenaphthylene in the monomer mixture	Other monomer	Estimated weight % acenaphthylene using absorption bands		
		295 or 298 mμ band	308 or 311 mμ band	Mean
10	Styrene	11.0	9.3	10.1
60	Styrene	61.8	59.2	60.5
80	Styrene	80.7	77.9	79.3
90	Styrene	96.1	94.9	95.5
10	Methyl methacrylate	9.8	8.3	9.1

Table III gives the acenaphthylene content calculated directly from the experimentally observed E values with the Beckman instrument at the maxima using polyacenaphthylene as standard and neglecting the shift in wave length.

As in these cases the polymerization was carried as near to completion as possible; the values in columns 1 and 5 in Table III show that figures of the correct order of magnitude can be obtained by means of the ultraviolet absorption spectra.

We wish to thank Dr. M. H. Khundkar for determining the spectra with the quartz Beckman Spectrophotometer.

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Synopsis

The strong ultraviolet absorption in the wave-length region 280-330 mμ shown by copolymers of acenaphthylene with styrene or methyl methacrylate is due to acenaphthylene residues. The spectra of samples of copolymer containing a small percentage of acenaphthylene are different from the spectrum of polyacenaphthylene. As a result of the comparison of the spectra of these copolymers with the spectra of acenaphthene and with the two forms of 1,1'-biacenaphthyl it is concluded that spectra of the copolymers can be explained as arising from the presence of pairs of acenaphthylene groups. Finally it is shown that the spectra can be used to estimate the acenaphthylene contents of the copolymers.

Résumé

L'absorption intense, que présentent les copolymères de l'acénaphtylène et du styrène ou du méthacrylate de méthyle dans la région ultraviolette du spectre, aux longeurs d'onde 280-330 mμ , est par suite des fragments acénaphtyléniques. Les spectres d'échantillons de copolymères, ne contenant qu'un faible pourcentage d'acénaphtylène, sont différents du spectre du polyacénaphtylène. Par comparaison des spectres de ces copolymères avec le spectre de l'acénaphtène et avec les spectres des deux formes du 1,1'-bisacénaphtyle, on conclut que l'explication des spectres des copolymères réside dans la présence de paires de groupes acénaphtyléniques. Enfin, les spectres d'absorption peuvent également être utilisés pour évaluer la teneur en acénaphtylène au sein des copolymères.

Zusammenfassung

Die starke ultraviolette Absorption im Wellenlaengebereich von 280-330 mμ , die in Mischpolymerisaten von Azenaphthylen mit Styrol oder Methakrylsaeure Methylester beobachtet wird, ist den Azenaphthylenkettengliedern zuzuschreiben; die Spektren von Mischpolymeri-

satsproben, die einen kleinen Bruchteil von Azenaphthylen enthalten, sind von Spektrum von Polyazenaphtylen verschieden. Durch Vergleiche der Spektren dieser Mischpolymerisate mit dem Spektrum von Azenaphthen und der beiden Formen von 1,1'-Biazenaphthyl wird geschlossen, dass die Spektren der Mischpolymerisate durch das Vorhandensein von Azenaphthylengruppenpaaren gedeutet werden kann. Es wird schliesslich gezeigt, dass die Spektren zu Schaetzung des Azenaphthylengehaltes der Mischpolymerisate verwendet werden koennen.

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Determination of Disappearance of Bis-isopropyl Xanthogen ("Dixie") in Synthetic Rubber Latex during Polymerization[1]

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Bis-isopropyl xanthogen ("dixie") has been used in the polymerization of synthetic rubber latex, either alone or with a mercaptan. When used alone, dixie is a poor promoter but an active modifier. Polymerizations with dixie in the standard recipe without mercaptan are poorly reproducible. The rate of conversion depends greatly upon the purity of the chemicals used (especially potassium persulfate and soap). Bis-isopropyl xanthogen seems to act both as a chain transfer agent and also as a retarder (chain breaker).

When dixie is used in a recipe with a higher molecular weight mercaptan the rate of conversion becomes quite reproducible, although dixie acts like a mild retarder in the presence of mercaptan. A polarographic method of the analysis for "dixie" in latex has been developed and is described in this paper. The disappearance of dixie was investigated, employing the "standard" recipe and using dixie with a mercaptan. The "standard" recipe was composed of butadiene 75, styrene 25, "dixie" (variable), potassium persulfate 0.3, soap (S.F. flakes) 5, water 180.

POLAROGRAPHIC METHOD FOR DETERMINATION OF DIXIE IN LATEX

Dixie is reduced at the dropping mercury electrode. The current-voltage curve of dixie in a 90% ethanol-0.1 *N* sulfuric acid medium shows a half-wave potential of about -0.15 volt versus the saturated calomel electrode, denoted below as S.C.E. and a well defined diffusion current at about -0.5 volt. In the above medium a distinct maximum is found in the polarogram before the diffusion-current is attained. On the other hand, if GR-S latex prepared by the standard recipe is coagulated in ethanol and dixie is then added, no maximum is observed. A maximum suppressor for dixie in ethanol solutions was sought. It was found that lauryl disulfide suppresses the maximum. However, it also appreciably suppresses the diffusion current of dixie.

In GR-S latex prepared with lauryl mercaptan (0.5 part), about 5% of the mercaptan is oxidized into its disulfide. Thus, if 8 grams of GR-S latex is coagulated in 90 ml. of ethanol the disulfide concentration in the solution will be approximately 0.0008%, if the original charge contained 0.5% DDM (dodecyl mercaptan).

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[1] This work was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Synthetic Rubber Program of the United States Government.

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The effect of the concn. of lauryl disulfide upon the diffusion current of dixie was determined as follows. A solution of dixie having a concentration of 15.0 mg. per 100 ml. in a 0.1 *N* sulfuric acid-ethanol-water (10% water) solution was placed in a polarographic cell, nitrogen (saturated with respect to 90% ethanol) was passed through for 30 minutes, and a polarogram was taken. Successive small amounts of lauryl disulfide solutions (in ethanol) were added and polarograms taken after nitrogen was passed through. The diffusion currents at -0.5 volt (vs. S.C.E.) were measured and are given in Table I, together with the dixie concentrations and the (calculated) ratio of microamperes to mg. of dixie per 100 ml. The measurements were carried out in a thermostat at 25°C.

The results show that at concentrations of lauryl disulfide between 0.0002% and 0.001% constant values of the diffusion current constant of dixie are found. The disulfide concentration after coagulation according to the recommended procedure in ethanol of a GR-S latex prepared with 0.5% DDM is roughly 0.0008% and would seem to satisfy the requirement that neither too little nor too much disulfide be present. In all the work described below, the lauryl disulfide concentration in the unknown solution was kept between 0.0002% and 0.001%.

After alcohol coagulation of latices in which mercaptan is present, an anodic wave is obtained at potentials of about -0.1 volt vs. S.C.E. in acid solutions. A wave at that point is undesirable. This wave was eliminated by the addition of a small amount of silver nitrate to precipitate the mercaptan.

Another difficulty encountered was an anomalous wave due to persulfate obtained when GR-S latex was coagulated in ethanol and the solution was made 0.1 *N* in sulfuric acid and 10% in water. When hydroxylamine hydrochloride was added and the solution heated the anomalous wave was eliminated. The hydroxyl amine reduces the persulfate.

A great number of unreported experiments has been carried out which showed that according to the recommended procedure normal dixie waves were obtained and that the diffusion current was proportional to the concentration.

TABLE I. Suppression of Dixie Diffusion Current by Lauryl Disulfide. Electrolyte: 0.1 N H_2SO_4-Ethanol-Water (10% Water). Readings Taken at -0.5 volt vs. S.C.E.

Concentration of dixie, mg./100 ml.	Concentration of lauryl disulfide, mg./100 ml.	Ratio: $\frac{\text{microamperes}}{\text{mg. dixie per 100 ml.}}$
15.00	0.0	0.286
14.95	0.1	0.283
14.91	0.2	0.274
14.87	0.5	0.273
14.82	1.0	0.271
14.75	3.0	0 263
14.64	10.	0.263

METHOD FOR POLAROGRAPHIC DETERMINATION OF DIXIE IN LATEX

The following procedure was found to give reliable and reproducible results:

Reagents Used

Absolute ethanol
10 *N* sulfuric acid
10% silver nitrate solution
20% hydroxylamine hydrochloride solution (in water)
1% lauryl disulfide solution in acetone

Apparatus

Measurements were made conveniently with a recording polarograph. The Heyrovsky polarograph, model XI, was used in the present work.

Procedure

Coagulate a weighed amount of latex, 5 to 10 grams, by adding it dropwise to 90 ml. of vigorously stirred ethanol. Add with continued stirring 1 ml. of 10 *N* sulfuric acid, 2 drops of silver nitrate solution (more if much mercaptan is present), one drop of lauryl disulfide solution and after a minute 6 drops of hydroxylamine hydrochloride solution. Heat the solution to boiling and boil gently for 2 minutes. Transfer to a 100 ml. volumetric flask, add sufficient water to make the total water concentration 10% and add ethanol to make the total volume 100 ml. (a small error, not greater than 2% is introduced here by not allowing for the volume of the rubber. This error tending to make the results slightly high is compensated by the slightly incomplete extraction.) Place a portion of this solution in the cell, pass nitrogen through for 30 minutes to remove oxygen and make a polarogram (either manually or with the self-registering apparatus). Measure the current at -0.5 volt. The diffusion current is determined by subtracting the residual current; i.e., the current obtained from a sample containing no dixie but treated as described above. From a previously determined relation between diffusion current and dixie concentration the dixie concentration in the unknown can be calculated.

Completeness of Extraction of Dixie from Latices

The completeness of extraction of dixie from a latex was investigated. Dixie was added to a 12 hour GR-S latex and the sample analyzed for dixie by the method described above.

The GR-S latex containing added dixie was prepared as follows: A weighed amount of dixie (about 100 mg.) was dissolved in a small weighed beaker in 2 ml. of ether, transferred to 100 g. of a regular 12 hour GR-S latex (prepared at 50°C.) containing no dixie. The mixture was shaken vigorously. The dixie left in the beaker was determined by drying and weighing. Then by weighing the latex containing the ether solution of dixie, the concentration of the dixie in the latex was calculated. The ether solution did not coagulate any of the latex.

Data concerning the completeness of extraction are given in Table II. The results indicate a satisfactory dixie recovery.

TABLE II. Extraction of Dixie from Latex

Sample	Sample weight, g.	Amt. of added dixie per g. latex, mg.	Dixie recovered, mg.	Dixie added, mg.	Dixie recovery, %
1	7.97	1.010	7.85	8.05	97.5
2	9.99	1.010	9.62	10.09	95.3
3	5.50	.998	5.65	5.49	97.2
4	6.42	.998	6.11	6.23	98.1

Polymerization with Mixtures of Dixie and a Mercaptan

Polymerizations were made according to the formula of the standard recipe given at the end of the first section, but using mixtures of dixie and a mercaptan. Charges of 100 g. were rotated in a thermostat at 50°C. for a specified time, cooled and analyzed for percentage conversion and for the amount of dixie and mercaptan remaining.

The percentage conversion was determined by evaporating a small sample of the latex to constant weight in a shallow dish at 110°C. (using a few crystals of hydroquinone as a short stop). From the weight of the residue is subtracted an amount corresponding to the soap persulfate, mercaptan and dixie content of the latex.

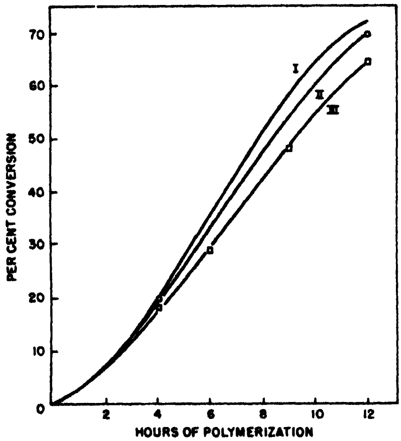

Fig. 1. Polymerization using n-octadecyl mercaptan as modifier: (I) 0.5 part DDM per 100 parts monomer, no octadecyl mercaptan; (II) 0.1 part octadecyl mercaptan per 100 parts monomer, no DDM; (III) 0.5 part octadecyl mercaptan per 100 parts monomer, no DDM.

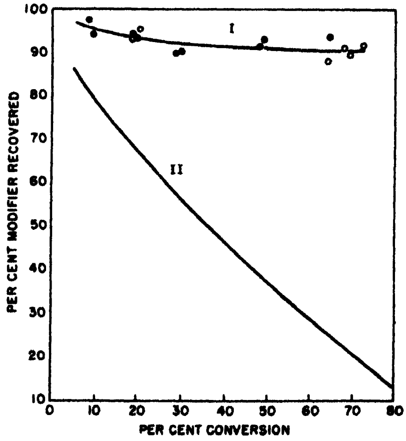

Fig. 2. Mercaptan consumption during polymerization: (I, ●) 0.5 part octadecyl mercaptan per 100 parts monomer; (I,○) 0.1 part octadecyl mercaptan per 100 parts monomer; (II) 0.5 part DDM per 100 parts monomer.

Mercaptan was determined by the amperometric titration method of Kolthoff and Harris (1) with silver nitrate. In experiments where octadecyl mercaptan was present, this method was modified slightly. Octadecyl mercaptan is only sparingly soluble in ethanol. In n-butanol it is very soluble even when diluted with 10% water. Therefore, the coagulation of the latex was performed in n-butanol. The percentage extraction of octadecyl mercaptan using this method was 98%, whereas methanol, ethanol, isopropanol and acetone gave less than 70% extraction of octadecyl mercaptan from latex.

Dixie was determined by the method described.

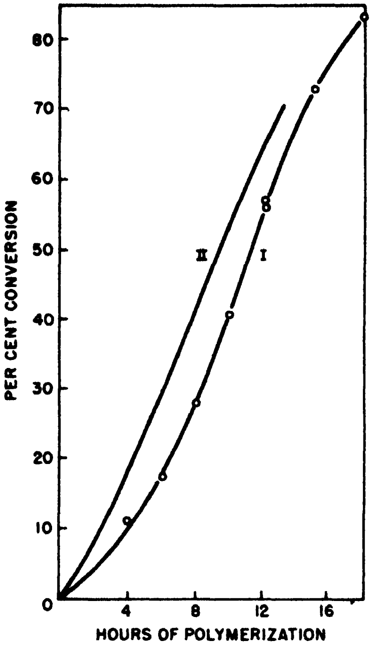

Fig. 3. Rates of conversion using a mixture of 0.5 part octadecyl mercaptan and 0.3 part dixie per 100 parts monomer (Curve I). Curve II: dixie omitted.

A. Mixtures of Octadecyl Mercaptan and Dixie. Octadecyl mercaptan is a poor modifier but a good promoter in the standard recipe although slightly lower conversions are found than with dodecyl mercaptan (DDM). This is evident from the curves in Figure 1 where the percentage conversion is plotted against hours of polymerization at 50°C. In Figure 2 is plotted the percentage of mercaptan consumed against the percentage conversion (cf. reference 1). After 70% conversion 90% of the octadecyl mercaptan remains unreacted.

Polymerizations were made according to the standard recipe using mixtures of octadecyl mercaptan and dixie as modifiers. Two different mixtures were used: 0.5 part octadecyl mercaptan; 0.3 part dixie and 0.1 part octadecyl mercaptan; 0.3 part dixie.

The rates of polymerization with these two mixtures are plotted in Figures 3 and 4. Also plotted is the rate of conversion for the same

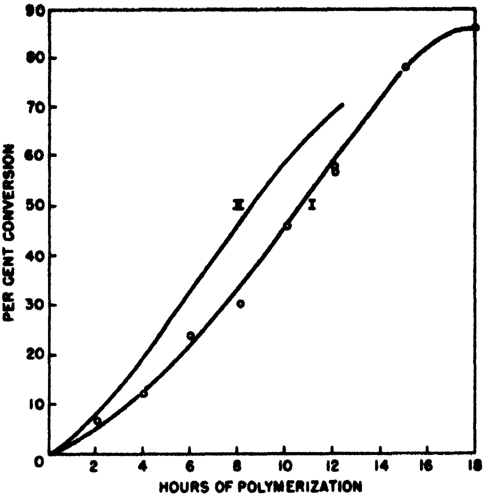

Fig. 4. Rate of conversion using a mixture of 0.1 part octadecyl mercaptan and 0.3 part dixie per 100 parts monomer (Curve I). Curve II: dixie omitted.

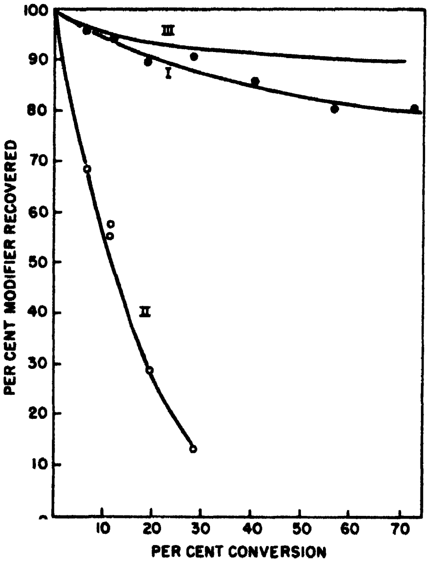

Fig. 5. Modifier disappearance using a mixture of 0.5 part octadecyl mercaptan and 0.3 part diisopropyl xanthogen per 100 parts monomer; (I) octadecyl mercaptan in mixed modifier; (II) dixie in mixed modifier; (III) octadecyl in absence of dixie.

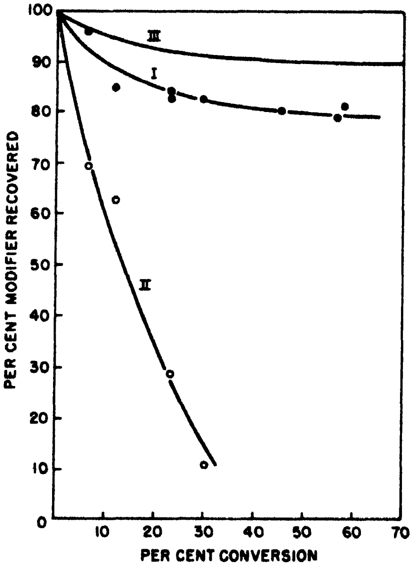

Fig. 6. Modifier disappearance using a mixture of 0.1 part octadecyl mercaptan and 0.3 part diisopropyl xanthogen per 100 parts monomer: (I) octadecyl mercaptan in mixed modifier; (II) dixie in mixed modifier; (III) octadecyl mercaptan in absence of dixie.

concentration of octadecyl mercaptan without dixie. In Figure 3 the rate of conversion is given with a mixture of 0.5 part of octadecyl mercaptan and 0.3 part of dixie (per 100 parts monomers). For comparison, the curve with 0.5 part octadecyl mercaptan alone is also given. It is seen that dixie retards the polymerization which is obtained with octadecyl mercaptan alone. This retardation is especially pronounced during the early stages of the polymerization. After 25-30% conversion the retarding effect of the dixie disappears. A similar result is found in polymerizations carried out with a mixture of 0.1 part octadecyl mercaptan and 0.3 part dixie, as shown in Figure 4.

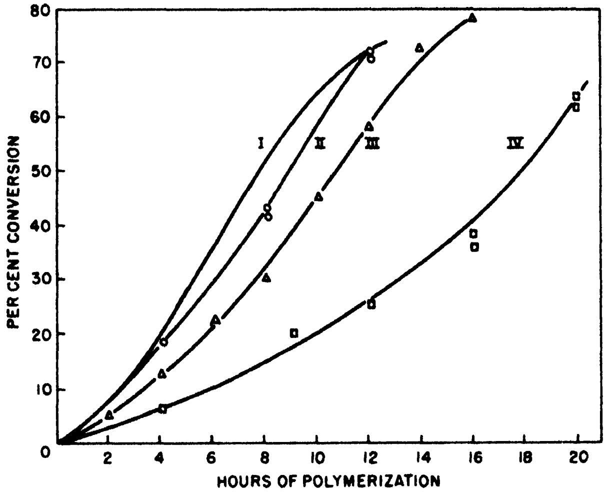

Fig. 7. Rate of conversion using 0.5% DDM and varying amounts of dixie: (I) no dixie; (II) 0.1 part dixie per 100 parts monomers; (III) 0.5 part dixie per 100 parts monomers; (IV) 2.0 parts dixie per 100 parts monomers.

In addition to the conversion, the mercaptan and dixie disappearance curves were also determined. These are given in Figures 5 and 6. It is seen that at the same conversion the disappearance of the octadecyl mercaptan is slightly greater when dixie is present than when it is absent. Dixie disappears very rapidly during the polymerization. After 30% conversion only 2% of the dixie is left.

B. Mixtures of DDM (Dodecyl Mercaptan) and Dixie. The effect of dixie upon the rate of conversion when added to the standard recipe charge with 0.5% DDM is very much the same as when the DDM is substituted with octadecyl mercaptan. Again the retardation is very pronounced during the first 30% of polymerization and thereafter the rate of polymerization is almost the same as in the standard recipe (see Fig. 7). The degree of retardation increases with the dixie concentration. Also, at 30% conversion less than 10% of the dixie remains unreacted. As with octadecyl mercaptan, it is found that the DDM consumption at the same conversion is greater in the presence of dixie than in the absence of dixie (see Fig. 8).

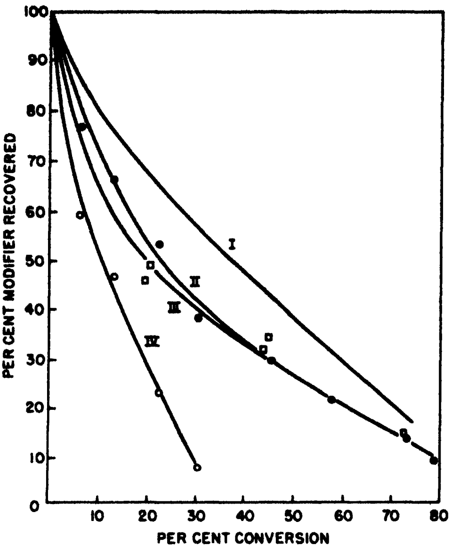

Fig. 8. Modifier consumption using a mixed modifier of 0.5 part DDM and 0.1 or 0.3 part diisopropyl xanthogen per 100 parts monomer. Modifier vs. conversion curves: (I) DDM curve, no dixie present; (II) DDM curve, 0.1% dixie present; (III) DDM curve, 0.3% dixie present; (IV) dixie curve, 0.3% dixie present.

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Synopsis

Bis-isopropyl xanthogen ("dixie") is a poor promoter, but an effective modifier, in the GR-S recipe, as was concluded from unreported intrinsic viscosity measurements. High molecular mercaptans are good promoters but very poor modifiers. In recipes containing mercaptans as promoters, dixie acts like a retarder until a conversion of 30% is attained. After this conversion the rate becomes normal. It is found that at a conversion of 30% most of the dixie has been dissipated. Bis-isopropyl xanthogen can be determined polarographically. A procedure is given for the polarographic determination of dixie and the determination by amperometric titration of mercaptan when both dixie and mercaptan are present in a GR-S latex. Disappearance curves of dixie and of mercaptans are given when both modifiers are present in the original charge.

Résumé

Le xanthogénate de bis-isopropyle ("dixie") est un promoteur faible, toutefois un régulateur efficace dans le mode de préparation du GR-S, ainsi qu'il résulte de mesures de viscosités intrinsèques non

publiées. Les mercaptans de poids moléculaire élevé sont de bons promoteurs, par contre, des régulateurs très faibles. Le "dixie," utilisé dans des modes de préparation, contenant également des mercaptans comme promoteurs, exerce un effet retardateur, jusqu'à l'obtention d'un rendement de 30%. Au delà de ce dernier rendement, la vitesse devient normale. On a trouvé qu'à ce moment la plus grande partie du "dixie" est consommée. Le xanthogénate de bis-isopropyle peut être déterminé polarographiquement. Un procédé de dosage polarographique du "dixie" est indiqué, de même qu'une détermination, par titrage ampérométrique, du mercaptan, lorsque à la fois le "dixie" et un mercaptan sont présents dans un latex GR-S. Les courbes de disparition du "dixie" et du mercaptan sont consignées, lorsque les deux regulateurs sont présents, à la fois, dans le mélange de charge initiale.

Zusammenfassung

Bis-Isopropyl xanthogen ("dixie") ist ein schwacher Promotor, aber ein wirksamer Modifikator in dem Buna-S-Rezept, wie aus unpublizierten Viskositaets-Zahlmessungen hervorgeht. Hochmolekulare Merkaptane sind gute Promotoren, aber sehr schwache Modifikatoren. In Rezepten, die Merkaptane als Promotoren enthalten, wirkt "dixie" als ein Verzoegerer, bis eine Umwandlung von 30% erhalten ist. Spaeter wird die Umwandlungsgeschwindigkeit normal. Es wird gefunden, dass bei 30% Umwandlung der Grossteil des "dixie" verbraucht ist. Bis-Isopropylxanthogen kann polarographisch ermittelt werden. Eine Anleitung zur polarographischen Ermittlung von "dixie" und zur amperometrischen Titrierung von Merkaptan—wenn sowohl "dixie" als auch Merkaptan in dem Buna-S-Latex enthalten sind—wird angegeben. Verschwindungskurven von "dixie" und Merkaptan werden gegeben fuer den Fall, dass beide Modifikatoren im Originalrezepte enthalten sind.

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REVIEW

"Elastomers and Plastomers, Their Chemistry, Physics and Technology, Volume II, Manufacture, Properties and Applications." Edited by R. Houwink, Elsevier, New York-Amsterdam, 1949, 531 pp., $9.00.

Nineteen authors of several nationalities have collaborated in the preparation of this comprehensive book. In any text of this type, dealing with a variety of somewhat independent facts, it is always difficult to arrange an orderly nonoverlapping sequence of chapters and sections. In this respect the various authors, under the editorship of R. Houwink, have been most successful.

The presentation of the subject is largely factual and there is little space devoted to historical or 'popular' discussions. Technical information is stressed throughout the text as in evidenced by many patent references and by the liberal use of flow sheets, diagrams, and photographs of items of practical interest.

The contents are separated into thirteen sections: (1) Phenol-Formaldehyde Plastomers by Houwink, Phenol-Formaldehyde Plastomers for Varnishes, Paints, and Lacquers by C.P.A. Kappelmeier; (2) Synthetic Resin Ion Exchangers by A. van Royen; (3) Urea and Melamine Resins by G. Widmer and K. Frey; (4) Polymers from Ethylene Derivatives by H.T. Neher; (5) The Cellulose Derivatives by V. E. Yarsley, H. Kitchen, and W.J. Grant; (6) Protein Plastics, Part I, Protein Plastics Other Than Fibres by A.D. Whitehead and S. H. Pinner—Part II, Fibers from Proteins by C. Diamond; (7) Synthetic Polyamides by L.E. Salisbury; (8) Silicone Polymers by J.R. Elliott; (9) Alkyd Resins by J.R. Patterson; (10) Natural Resins and Their Derivatives by I.C. Clare; (11) Derivatives of Natural Rubber by T. R. Dawson; (12) Synthetic Rubbers by W.J.S. Naunton; and (13) Asphalts by R. N. Traxler.

In view of the important practical information contained in this text, it is highly recommended to active workers in the field.

Robert B. Mesrobian

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REVIEW

"Colloid Science, Vols. I and II." A. E. Alexander and P. Johnson. Oxford Univ. Press, London, 1949. 837 pp., $15.00

Since the appearance of Freundlich's famous treatise, there have been only a few general texts stressing the quantitative aspects of the science of colloids. The present two volumes by (former) members of the Department of Colloid Science at Cambridge represent a successful effort to produce such a work. It is their purpose "to meet the need for a modern treatment of colloidal systems, intermediate in level between the elementary, purely descriptive text books and the specialized accounts .... available in monographs and the 'recent advances' type of article...."

The presentation is divided into two parts, the second of which deals with specific colloidal systems. The first volume starts out with an historic survey. There follow chapters reviewing thermodynamic principles, their application to various pertinent problems, and a brief discussion of the Debye-Hückel Theory and the question of stability. More than half of the first volume is devoted to a detailed exposition of equilibrium and rate methods for the determination of mass, dimensions, charge, etc., of colloidal particles and large molecules and their theoretical basis. The final chapters deal with interfacial phenomena and contain sections on insoluble monolayers, adsorbed films and the solid-liquid interface. The special systems considered in the second volume are the customary ones except for a rather detailed discussion of proteins, a class of substances also extensively drawn upon for obvious reasons to illustrate general methods. There is also a survey of the main types of organic polymers and their behavior in solution.

Judging from the references included, the manuscript was completed in 1946. Some recent and important developments in several pertinent topics are therefore excluded.

It is only natural in a work of this breadth that the reader can detect omissions in references and subject matter. One wonders, for instance, why more recent studies on solutions of tobacco mosaic virus were barely mentioned or why at least a reference to modern theories of slow coagulation was not given. Also, in a treatise of this kind, one expects disagreement with the authors' presentation or conclusions on one or another occasion.

The student versed in physicochemical fundamentals, without being a specialist, will read the majority of the chapters with not more than the customary effort. However, there are some parts where this is not true and where the difficulty is not entirely due to the subject matter or to the necessity to be brief. For instance, will the unsuspecting reader obtain a clear picture of nonideal rheological behavior? In the chapter on solution viscosity, the enumeration of several equations, referring (seemingly) to the same physical situation, must leave some confusion and so will the interpretation of Staudinger's rule, even in 1946. Similar comments apply to the discussion of light scattering in two different places.

All this, however, does not detract from the intrinsic value of these two volumes for the student with the proper background and the active research worker wishing to obtain a survey of the potentialities of certain methods or the properties of certain colloidal systems. Particularly to these the book is heartily recommended.

Robert Simha

REVIEW

"Physics and Chemistry of Cellulose Fibres with Particular Reference to Rayon." P. H. Hermans. Elsevier, New York-Amsterdam, 1949. 556 pp., $7.50.

This book dealing with the physics and physical chemistry of cellulose fibers, develops throughout the general picture of cellulose as a three-dimensional mosaic of crystalline regions imbedded in amorphous regions with the individual cellulose chains passing alternately through several of these regions. Native and regenerated cellulose fibers are characterized in terms of optical, x-ray, density, sorptive, mechanical and fiber-morphology properties, as well as in terms of molecular properties, and all of these properties are interpreted in terms of the network structure. Methods are given for calculating orientation and degree of crystallinity from physical properties; however, this part is not easy reading like the rest of the book and not all the assumptions on which the calculations are based are made clear to the reader.

The last section covers the production of viscose rayon and the properties of the rayon in both the primary gel and final fiber state. The discussion of the viscose process is not extensive but it shows a keen insight into some of the basic problems of fiber production. The discussion of properties concerns largely the mechanism of deformation of the network structure with special emphasis on the effects of swelling in making the fiber more rubberlike.

The information in this book pertains largely to fields in which the author has done considerable work and on which he can write with authority. The large amount of detailed information and extensive reference make this book a valuable reference book for technologists and students interested in cellulose and other fibers. The reader will need to remember that not all significant literature on the subjects covered by this book is mentioned because of the unavailability to the author of the non-European literature up to 1947. The lack of information on the chemistry of cellulose prevents this book from being a textbook on cellulose.

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Influence of Activated Carbon on Styrene Polymerization

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Experiments on emulsion polymerization of styrene have indicated the possibility that the increase of styrene-water interface could play an important role in increasing the rate of polymerization (1). It should therefore be of some interest to study the influence of large surfaces on polymerization. Active carbon (2) is used for the experiments reported here as a bearer of the most likely "organic" surface. In particular, Rummel's experiments (3) on catalysis of parahydrogen transformation by active carbon have showed that at least in this case the catalytic action is due to the carbon surface itself and not to any contaminants.

For an initial survey, eight different active carbon preparations were employed. The carbons were air-dried at 200°C. and placed into reaction bottles containing styrene at room temperature, under nitrogen. The reaction bottles were then freed of gases and sealed in vacuo.

The styrene samples were polymerized by heating in a constant temperature bath for three hours at 90°C. with continuous shaking.

The determination of polymer yield was rather difficult, since the highly dispersed activated carbon adhered tenaciously to the polymer. However, a satisfactory separation was usually obtained by centrifuging the solutions. In Table I are given the results of these experiments.

TABLE I. Polymerization of Styrene in Presence of Active Carbon

Sample No.	Source	Quality	Polymer yield, %	Intrinsic viscosity,[a] [η]
None	-	-	3.0	0.20
1	"Carbo spongiae"	Powder	0.008	--
2	"Carbo ossium" (granulated)	Fine grained	0.15	0.08
3	"Gasmasken kohle"	Coarse grained	2.3	0.34
4	"Carbo sanguin acido depurat"	Powder	0.41	0.07
5	-	Powder	0.05	--
6	-	Coarse grained	0.76	0.25
7	Cane sugar carbon	Fine grained	2.4	0.16
8	-	Powder	0.24	0.06

[a] Concentration: g./liter.

All the carbon preparations examined decreased the rate of polymerization to some extent. Those having considerable retarding effects also decreased the intrinsic viscosities of the polymers. On the other hand, those carbons which were less effective reducing the rate of polymerization produced polymers with higher intrinsic viscosities than were obtained in the control polymerization (without active carbon). The latter must then be considered to increase the average degree of polymerization and to produce a "chain lengthening effect."

TABLE II. Influence of Purification and Shaking Speed

Treatment of carbon sample (Carbon No. 4, Table 1)	Polymer yield after 3 hrs. at 90°C. %
Heated in air at about 200°	0.24
Heated in hydrogen at about 600°C.	0.15
Heated in nitrogen at about 600°C.	0.38
Heated in air at about 200°C. shaken slowly	0.09
Heated in air at about 200°C. shaken rapidly	0.09

In the following more detailed experiments two different carbons were used; sample 4 (Table I), which gives a typical retarding effect, and sample 3, which gives the greatest increase in viscosity.

Both of these carbons were purified by extracting first with water and then - after drying - with toluene. The carbon samples were then heated in reaction bottles under high vacuum and freed of gases. Styrene was next distilled into the reaction bottles under vacuo. All of the oxygen adsorbed at the carbon surface is not entirely removed, however, by this treatment.

TABLE III. Polymerization at 90°C.[a]

Time of reaction, hr.	Polymer yield, %	Intrinsic viscosity,[b] [η]
2	0.11	0.05
5	0.22	0.11
10	0.40	0.25
20	9.40	0.41

[a] 0.2 g. carbon sample 4 with 2 cc. styrene.
[b] Concentration: g./liter.

In order to determine the influence of residual oxygen, experiments were carried out with a carbon sample which was heated for a considerable time at 600°C. under hydrogen before introducing it into the reaction bottles. Experiments were also carried out to determine the effect of shaking speeds. The carbon samples used (Table II) were treated with alkali before extraction.

The results given in Table II were chosen as typical as samples of a greater number of experiments. Although they show certain irregularities, it seems evident that the retarding effect is caused by the added carbon and not by adsorbed oxygen or any other contaminants.

TABLE IV. Polymerization at 90° C. with Carbon Sample 3

Grams of carbon sample 3 in 2 cc. styrene	Time of polymerizations, hours	Polymer yield, %	Intrinsic viscosity,[a] [η]
0.2	1	0.76	0.26
0.2	3	1.80	0.36
0.2	5	1.21	0.46
0.2	7	2.09	0.44
0.2	10	6.77	0.36
0.1	0.5	0.52	0.21
0.1	1	0.68	0.27

[a] Concentration: g./liter.

The next important problems were to specify whether or not the observed effects resulted from a catalytic acceleration of the chain termination step, or, if the active carbon loses its efficiency during retardation; and to compare this action with that of standard retarders (quinones, etc.) present in a homogeneous reaction. For these studies, the action of the active carbon was followed throughout a considerable period of time.

The results of Table III clearly indicate that the carbon has only a limited retarding effect, which completely disappears after about eleven hours. Furthermore, it is observed that as the reaction proceeds the carbon tends to increase the intrinsic viscosity of the polymer formed until greater values than that for the control polymerization are reached (Table III).

TABLE V. Adsorption of Polystyrene from Toluene

Sample No.	Temperature, °C.	Concentration of solution, g./liter: Before adsorption	Concentration of solution, g./liter: After adsorption	Intrinsic viscosity[a] of dissolved polymer: Before adsorption	Intrinsic viscosity[a] of dissolved polymer: After adsorption
3	50	7.66	--	0.167	0.161
3	90	9.92	10.36	0.171	0.163
4	20	6.78	6.64	0.163	0.169
4	50	8.86	9.20	0.166	0.160
4	90	7.60	7.54	0.163	0.166

[a] Concentration: g./liter.

In addition to the retarding effect, it is evident the active carbon tends to promote longer chains. To study this lengthening effect, several experiments with carbon sample 3 were carried out (Table IV).

It may be seen that the lengthening effect, as well as the retarding effect, are limited to the earlier times of reaction only.

The next problem was to determine whether or not the carbon is able to react with the "dead" polymers, since considerable adsorption of polymer to the carbon could invalidate the observed results.

An unfractioned polystyrene (intrinsic viscosity 0.17) polymerized at 100°C. was dissolved in toluene and shaken with two active carbons for three hours at various temperatures (Table V).

It should be noted that the carbon does not increase the viscosity of the "dead" polymers. Also, within the limits of error, no adsorption of polymer takes place. Therefore the viscosity increasing effect, as well as the polymerization rate retarding effect, which we have observed, must be related only to some form of reactivity of the growing "alive" polymer.

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Synopsis

During a definite polymerization time the rate of uncatalyzed polymerization of styrene may be decreased by the use of activated carbon. The intrinsic viscosities of the polymers formed may be either increased or decreased by the addition of active carbon, depending upon the activity of the carbon sample used.

Résumé

Au cours de la polymérisation du styrène, en absence de catalyseur il est possible de faire décroître la vitesse de polymérisation en utilisant du charbon actif. Les viscosités intrinsèques des polymères formés peuvent être soit augmentées soit diminuées par addition du charbon actif, suivant l'activité du charbon utilisé.

Zusammenfassung

In einer gegebenen Polymerisationszeit kann die Geschwindigkeit der unkatalysierten Styrolpolymerisation durch aktivierte Kohle verringert werden. Die Viskositaetszahlen der Polymerisate koennen durch den Zusatz aktivierter Kohle vergroessert oder verringert werden, je nach der Aktivitaet der benuetzten Kohle.

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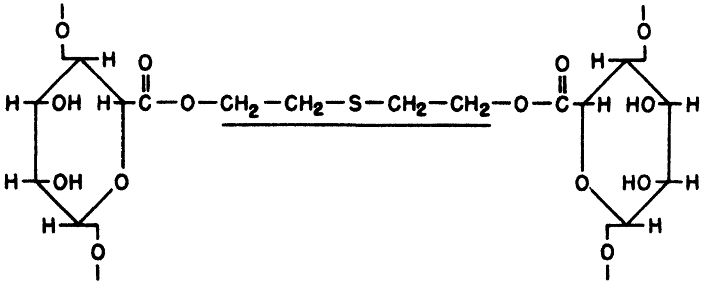
LETTER TO THE EDITORS

CROSS LINKING OF SODIUM ALGINATES BY MUSTARD GAS

The chemical and physiological properties of mustard gases were studied very intensively during the last war (1,2). These compounds are highly reactive, for example, organic sodium salts in aqueous solution readily form thio-diglycol esters with mustard gas (3). The high reactivity of mustard gases is believed to depend on their ability to form unstable three-membered rings (ethylenesulfonium or ethylenimonium ions). The toxicity of these compounds is explained by their reactivity with the functional groups of biologically important body substances, especially proteins and nucleic acids (1,2,4).

Di-(β -chloroethyl)-sulfide, being a bifunctional compound, may react with two functional groups either of a single molecule or of two molecules. In the case of chain molecules with easily accessible reactive groups, cross linking between the macromolecules should be possible. A reaction of this type was observed by Elmore et al. (5) in their experiments with nucleic acids. Goldacre, Loveless, and Ross (6) have recently advanced the hypothesis that the cytotoxic effects of mustard gases are due to cross linking of the chain molecules in the chromosomes. According to Lautsch (7) it is possible to bring about cross linking between lignin and polyethylenimine by reacting them with di-(chloroethyl)-methylamine.

Cross linking by mustard gas can easily be demonstrated with sodium alginates, pectates and pectinates:



Thio-diethylene bridge between two alginic acid chain molecules

After addition of mustard gas to dilute aqueous solutions of these high molecular compounds a rapid increase in viscosity takes place, and finally primary valence gels are formed. Furthermore, because of the rapid hydrolysis of mustard gas, mono-esters and thio-diglycol are also produced. Di-epoxides containing two three-membered rings react in a similar manner with high molecular acids. Here too, under favorable conditions, gel formation can be brought about (8).) From the sulfur content of the reaction products and from the amount of esterified carboxyl groups it is possible to calculate the number of bridges formed. By alkaline saponification the three-dimensional gel network is destroyed.

With increasing degree of esterification of alginic acid (glycol esters) and pectic acid (methyl esters, pectins) the tendency to gel on addition of mustard gas decreases. Gelification also depends on the chain length, as would be expected. This could be shown with different preparations of alginic acid obtained by acidic degradation. The lower the molecular weight of the alginic acid, the higher the concentration must be in order to induce gelification. (A degradation of alginic acid by mustard gas could not be detected.)

TABLE I. Gelification of Aqueous Solutions of Sodium Alginates (0.8%) by Increasing Amounts of Mustard Gas (η_{sp}/c of the alginic acid in 0.05 N NaOH at 20°C.= 6.23; c = 1 millieq./100 cc.)

Concentration of mustard gas, %	Setting time, minutes
0.1	180
0.3	30
0.5	10
1.0	5

TABLE II. Gelification of Aqueous Solutions of Sodium Alginates of Different Chain Length. (Concentration of Mustard Gas 0.22%.)

η_{sp}/c of Na alginates	Minimum conc. of Na alginate, %, for gelification within 4 hours
6.23	0.08
1.51	0.61
1.15	1.35
0.77	2.15
0.39	2.46

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LETTER TO THE EDITORS

STRETCHING OF DISSOLVED CHAIN MOLECULES BY THE INTRODUCTION OF SIDE GROUPS

The shape of chain molecules in solution is not fixed, due to the free rotation of single bonds of the type C-C, C-O, etc. (1). Factors which restrict this rotation usually cause a stretching of the molecule. Some of these factors are: uncoiling in a streaming solution (2), solvation (3) and electrostatic repulsion between dissociated groups within the same macromolecule (4). Rotational restriction may also result from side groups introduced into the molecule. Stretching of the chains can be detected by an increase in viscosity and in birefringence of flow. This steric effect can be demonstrated with aqueous solutions of pectic or alginic acid esters containing easily removable side groups.

Esterification of alginic acid with ethylene oxide yielded the glycol monoester (5). The ester was saponified in aqueous solution by the addition of NaOH without any degradation taking place. By this method different neutral sodium salts with a degree of esterification varying between 100% and 0% were prepared. The viscosity of the aqueous solutions (Table I) increases with increasing degree of esterification. This effect is only slightly diminished at higher temperatures. Table I shows that at 20°C. η_{sp} of the fully esterified preparation is nearly three times that of the completely saponified sodium alginate. It should be stressed that the observed increase in viscosity is not due to a higher solubility of the totally esterified product. Rather, this increase in viscosity may be explained by the restriction of rotation of the glycosidic linkages, which occurs on the introduction of bulky side groups and causes stretching of the chain. It is interesting to note that the viscosity increment of the -COOR groups is higher than that of the dissociated -COONa groups.

A similar increase in viscosity has been observed with aqueous solutions of methyl (6,7) and glycol esters (5) of pectic acid. It may be assumed that a stretching of the chain molecule influences other properties too. It is possible that the greater rigidity of the more highly esterified pectin molecules is partially responsible for their better gelling properties. The dependence of the rate of enzymatic hydrolysis on the degree of esterification (8) may also be explained by assuming that the glycosidic linkages are blocked by the ester groups. Not only are the more highly esterified pectins hydrolyzed more slowly, but the mechanism of enzymic attack is also different. Here the degradation seems to advance from the ends of the chains, rather than commencing at random points throughout the molecule.

TABLE I. Specific Viscosities of Aqueous Solutions of Glycol Monoesters of Alginic Acid with Different Degrees of Esterification (Concentration of the Solutions: 1.6 millieq. alginic acid/100 cc.)

Temp., °C.	Degree of esterification, %				
	0	25	50	75	100
	Specific Viscosities η_{sp}				
20	1.29	1.69	2.04	2.90	3.44
40	1.11	1.42	1.74	2.36	2.69
60	0.89	1.14	1.37	1.90	2.03
80	0.72	0.90	1.05	1.34	1.43

Short side groups may be expected to influence similarly the shape of other dissolved chain molecules. The high viscosity and birefringence of flow of locust bean mucilage (7,9), for example, may be caused among other things, by the galactose side groups, scattered along the polymannose chain (10).

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LETTER TO THE EDITORS

INTERACTION BETWEEN POLYMERS AND FILLERS[1]

In the literature the problem of whether or not the filler particles adhere to a polymer is still under discussion. This point is already of interest in the mixing process because here the question is resolved to: will the particles clog together or will each of them become separately surrounded by polymer only (1). The problem is also of paramount interest with regard to the properties of the final mixture because upon the interaction depends whether or not a filler will have a reinforcing action. This is a key problem especially in the rubber industry.

Essentially, the problem of dispersing a filler into a polymer is of the same type as that of dissolving a polymer in a solvent, and for the thermodynamic considerations we know (2) that dispersing will occur if (leaving the entropy factor out of discussion) ΔU(U = internal energy) is negative, that is, heat is liberated. Here the historical measurements of Hock and co-workers (3) show that, on mixing rubber with carbon black, 11 gcal. per gram of black (which is of the order of 1 gcal. per mole) extrapolated to zero concentration, are developed. This heat is found to decrease with increasing amount of filler, showing that all particles are no longer in contact with the rubber because of clogging. It has long been a problem to explain the outstanding reinforcing properties of carbon black with the aid of these low values found by Hock.

Smith and Shaeffer (4) showed that the initial heat of adsorption between carbon black and C_4 hydrocarbons is of the order of magnitude of 15 kcal. per mole, decreasing sharply until about 40% of a monolayer is formed. This indicates that 40% of the carbon black surface is covered with sites of high adsorptive capacity. Between 40 and 100% of this monolayer formation the surface appears to be quite uniform with regard to adsorptive capacity; at the monolayer the values again decrease and approach the heat of liquefaction, E_L, of the adsorbate. These results are shown in Figure 1. From the data obtained it can be derived that the heat of adsorption per CH_2 group to carbon black is about 4 kcal./mole.

In our opinion these step-by-step adsorption experiments are keys to the explanation of the reinforcing action of fillers. They make it clear that the integral heat of adsorption measured by Hock never

[1] Communication 108 of the Rubber Foundation, Delft, Holland.

could lead to a proper understanding of the fundamental background. There may be attractive and repulsive forces on the carbon black particle, leading to negative and positive heats of adsorption. What Hock measures is the algebraic sum of these values, and so one may even find a positive heat (repulsive sites preponderating), although adhesion takes place on the attractive spots. The measurements of Smith disclose the true situation and show that a limited number of attractive sites may be responsible for the reinforcing effect. It is important to note that part of these sites are of a relatively high energy content (15 kcal.), leading to strong bonds.

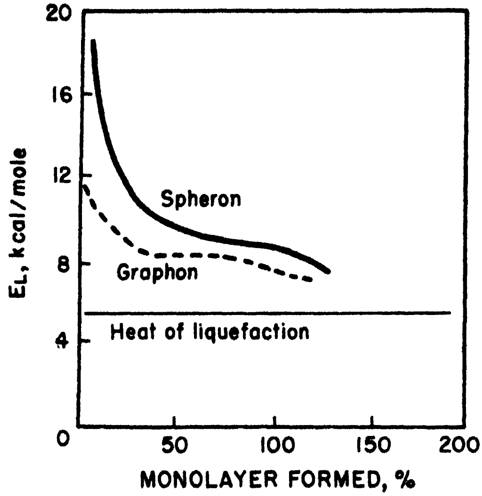

Fig. 1. Heat of adsorption between carbon black MPC and 1-butene (0°C.).

Such sites of high adsorptive capacity may be due to the attraction by certain atomic groups, but there exist also other factors leading to selective adsorption. de Boer and Custers (5) showed that in the case of adsorption of gases by means of van der Waals' forces the gain of energy is maximal when the molecule of the adsorbent can make a maximum number of contacts with the surface. Figure 2 shows the adsorption energies at various parts of a crystal, according to calculations by Kossel (6), from which it appears that the values in this simple case vary from 0.066 to 0.874, or by a factor of 13.

In contrast to this stands the adsorption by means of electrostatic forces, where the energy gain is maximal at sharp corners, sticking out of the surface.

If the surface of a normal crystal is observed microscopically it appears that no flat surface is actually present (6). Referring to the great number of crystallites (7) in a carbon black particle, an extremely uneven surface is to be expected here; one black particle may contain 1000 crystallites with a length between 15 and 30 A. So one may assume a spectrum of adsorptive forces. This spectrum will become still more complicated due to the different chemical composition of the surface at various spots. In this respect we refer to the presence of H, CH_3, COH, and COOH groups on one and the same carbon black particle.

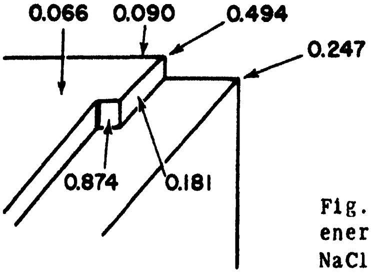

Fig. 2. Van der Waal's adsorption energies at various sites of a NaCl crystal.

Bearing in mind that carbon black is more or less a hydrocarbon, the conditions for wetting rubber will be favorable, but a less ideal situation may be expected for other fillers. However, there is too little known to make definite statements; there are even opinions (8) that any filler adheres well to rubber if only the right method of dispersion is applied and the adsorbed air films can be removed.

The negative heat of wetting of carbon black explains why unvulcanized rubber becomes insoluble in gasoline when adding black. The latter cannot be loosened from the rubber, since a physical bond is formed (9).

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LETTER TO THE EDITORS

SIDE-CHAIN COPOLYMERIZATION

The decrease in molecular weight of vinyl polymers when polymerized in the presence of chain transfer agents has been discussed at length, and an adequate explanation has been proposed. We will discuss here the possible nature of the products that would be obtained when the chain transfer agent is itself polymeric in nature. For simplicity, we will consider the case of a polymer fraction in which all chains are of length D, i.e., each chain contains exactly D monomer units of type A. When such a polymer is dissolved in a monomer B, chain transfer reactions will take place during the polymerization of B. As a result, the A polymer will have side-chain of B attached to it.

We have derived an expression for the number-fraction, N(r,m), of A polymer chains that contain r side chains of combined length m.

$$N(r,m) = [1 - (1-x)^K]^r \, (1-x)^{K(D-r)} \frac{D!}{(D-r)!\,r!} \, p^{m-r}(1-p)^r \frac{(m-1)!}{(m-r)!\,(r-1)!}$$

K is the chain transfer constant for the system, i.e., k_t/k_p, and x is the fraction of B polymerized. The propagation probability, p, is the ratio of the rate of propagation to the combined rates of propagation, transfer, and termination. This quantity does not change appreciably during the course of the reaction and has been treated as a constant.

The number fraction of A chains containing m attached B groups is then:

$$N(m) = \sum_{r=1}^{m} N(r,m) \qquad \text{for } m<D$$

$$N(m) = \sum_{r=1}^{D} N(r,m) \qquad \text{for } m>D$$

Finally, if all the A polymer with the attached side chains is separated from monomeric and pure polymeric B, the mole fraction of B in the side-chain copolymer is given by:

$$b = \frac{1 - (1 - x)^K}{2 - p - (1 - x)^K}$$

By an appropriate choice of materials and concentrations, it should be possible to prepare side-chain copolymers either with a few long side chains or many short side chains.

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REVIEW

"Elastomers and Plastomers, Their Chemistry, Physics and Technology," Volume III, "Testing and Analysis: Tabulation of Properties." Edited by R. Houwink, Elsevier, New York-Amsterdam, 1948. 174 pp., $4.50.

This book, the third of a three-volume series, discusses the testing and analysis of plastomers and elastomers from an entirely practical point of view. The theoretical background for most of the testing methods described here is presented in Volume I, and the discussion of properties in connection with application of the materials in Volume II.

Four authors, under the editorship of R. Houwink (Netherlands) have contributed to the writing of this book. The chapter on Methods of Testing is written by J. H. Teeple (U. S. A.) and represents a successful endeavor to survey the principal methods employed in the United States, Great Britain, Germany, and other countries. The chapter on Chemical Analysis of Polymers by A. G. Epprecht (Switzerland) is treated in a very systematic and complete way. An additional feature in this chapter is the rather large amount of original work presented by Epprecht necessary to cover this topic completely and which may not be found elsewhere. The last two chapters are essentially tabulations of the different properties of elastomers and plastomers derived from work carried out by B.B.S.T. Boonstra and J.W.F. van't Wout (Netherlands) in collaboration with the editor. The elastomers and plastomers are considered as two separate groups in view of the fact that they are characterized by different testing methods.

The book is well organized and contains all the details necessary to cover the subject matter. It is highly recommended for purchase by industrial polymer chemists, research laboratories, and reference libraries. In view of its practical nature, however, it is doubtful if it will be attractive to the student of polymer chemistry interested only in fundamental details.

Robert B. Mesrobian

REVIEW

"Proteins and Life" (Frontiers of Science Series). M. V. Tracey, Pilot Press, London, 1948, 154 pp., 10s 6d.

This book is an excellent introduction for the nonspecialist to proteinology, nutrition, chemical physiology, bacterial chemistry, and immunology. The text is up-to-date and contains a wealth of facts; the concise style makes it easy reading. Methods and theories are briefly but adequately explained, and the illustrations are well chosen. The specialist will probably find nothing new in the chapters dealing with his own field, but he may be benefited by the other chapters dealing with neighboring branches of science.

C. F. Jacobsen

REVIEW

"The Theory of Solutions of High Polymers." A. R. Miller, Oxford Univ. Press, London, 1948, 114 pp., $3.25.

It is now well known that the behavior of solutions of linear high polymers is markedly different from that of solutions of chemically analogous small molecules, also that these differences can be related to the combination of large size and chain structure of the high polymer molecules. In particular, it has been shown (by the reviewer and others) that the equilibrium properties of linear high polymer solutions – their vapor pressures, osmotic pressures, solubilities, etc.– can be approximately deduced theoretically by statistical calculations of the entropy of mixing of the components.

In this book the author gives an excellent presentation of the elegant methods of statistical thermodynamics developed by Fowler and Guggenheim and their application to this problem. To anyone interested in getting to the fundamentals of the subject or in further extension of the theory, this is valuable indeed. Inadequacies in the simple theory are brought out by comparison of some experimental data on rubber and polystyrene solutions with the theoretical results. Possible extensions of the theory are discussed briefly.

This is an important and useful addition to the scientific literature. It is, however, definitely written for the specialist in statistical thermodynamics; most others would find the extensive mathematical development not understandable or not interesting.

The author, publishers, and proofreaders should be commended for an especially fine job on the mathematical equations, since it is not easy to make sure that characters of the correct nationality (Greek, Roman, or Arabic), size, and slope are chosen and placed accurately in their proper relative locations.

Maurice L. Huggins

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REVIEW

"The Chemistry and Technology of Enzymes." Henry Tauber, Wiley, New York, 1949, 558 pp., $7.50.

This volume represents an expansion of an earlier book by the same author, entitled "Enzyme Technology." In the preface, it is stated that "this new book contains an up-to-date review of enzyme chemistry: methods concerning the industrial production of enzymes from all known sorces and their uses; the production of all the industrially important organic compounds by fermentation; and microbiological procedures for the quantitative determination of vitamins and amino acids."

Even a cursory examination of the book shows that it falls short of accomplishing such ambitious aims. In fact it would be almost physically impossible to treat such a vast subject in a detailed manner in such a limited space. However, a more serious defect appears to be a distinct lack of consistency and of critical evaluation of experimental data which was evident in the earlier book of the author. Thus, on the first page, the genes are considered as cytoplasmic units following Spiegelman and Kamen, in spite of the fact that the localization of the gene in the cell nucleus, and more specifically in the chromosomes, is at present generally accepted by practically all workers in the field and Spiegelman's hypothesis of "plasma genes" is widely considered untenable. On the same page, the enzymes are called "the agents that supply all living things with energy for work and for biosynthesis." While such poorly defined statements may be overlooked in a nontechnical treatise, they seem to be out of place in a serious treatment of such an important subject. It is one of the basic tenets of catalysis and enzyme chemistry that the catalyst does not supply any free energy to the system the reaction of which it promotes. There are, unfortunately, many other examples for the inconsistency in the treatment of the subject matter such as the sentence on pages 2 and 3: "Substances such as glutathione, ascorbic acid, cytochrome, and adenylic acid are not catalysts." Further down on the same page, cytochrome c is listed as "part of cytochrome c oxidase systems." In the same table, it is said that "the cytochromes are carriers of electrons. They are not enzymes." A serious omission, in the same table, is the failure to list cytochrome oxidase (Warburg's "respiratory enzyme") as one of the iron-porphyrin enzymes.

No table listing the various pyridinoproteins (enzymes requiring coenzymes I and II) is found in the book; the important enzyme uricase is not mentioned in the text.

The treatment of the chemistry and action-mechanism of catalase is also inadequate; the well-established fact that its prosthetic group is protoheme is ignored. No credit is given to Zeile for the fundamental discovery of the hemoprotein nature of this enzyme. It is also regrettable that not more than ten pages in Chapter XXII are devoted to the important subject of the production of enzymes using microorganisms, including bacteria and molds. It is well known that the large-scale production of enzymes by these means is a carefully guarded secret process in industry. The author is, in fact, not in the position to shed much light on the subject, and anyone looking to his book for detailed information on this point will be more or less disappointed.

Kurt G. Stern

REVIEW

"Monomers." Edited by E. R. Blout, W. P. Hohenstein, and H. Mark. Interscience, New York, 1949, 368 pp., $7.50.

This book which is the beginning of a series is an attempt to provide a convenient source of information about important monomers. Thus, under one heading, may be found procedures for preparation, also the purification, storing, handling, physical constants, reactions, and other pertinent data. There is no doubt that if the aims of the preface are carried out in succeeding series, this type of compilation will be of invaluable service to research and development in the polymer field.

This issue covers the monomers: acrylonitrile (Irving Waltcher), butadiene (Sylvia Polstein), isobutylene (Pnina Spitnik), isoprene (Pnina Spitnik), methyl methacrylate (Richard S. Corley), styrene (Sylvia Polstein), vinyl acetate (Paul Fram), and vinyl chloride (Harold Shalit). In most cases, an attempt has been made to critically evaluate which preparation or preparations are actually in commercial operation. No attempt has been made to evaluate completely or describe all the polymerization data concerning each of these monomers and this may be desirable as the emphasis is then centered on the preparation and properties of the monomers, since there are other varied sources of collected polymerization data.

The book has some errors in style. There are inconsistences; thus, chemical formulas are sometimes inserted for names in the running text.

As a serviceable source of information, I would recommend this compilation for the libraries of any research or engineering group engaged in polymer work.

C. G. Overberger

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